Guidance Document and Recommendations on the Types of Scientific Information to be Submitted by Applicants for California Fuels Environmental Multimedia Evaluations

Prepared for the
Multimedia Working Group by

The University of California, Berkeley

The University of California, Davis
and

Lawrence Livermore National Laboratory

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Table of Contents

I. Executive Summary

As required by Section 43830.8 California Health and Safety Code, before adopting new fuel specifications the California Air Resources Board (CARB) is required to prepare a "multimedia" evaluation and submit it to the California Environmental Policy Council for final review and approval. In general, the State of California needs information that will allow an informed decision as to the relative risk posed by any newly proposed fuel to the State's resources, human health and the environment. New fuels or potential additives must be evaluated not only with regard to engine performance and emission requirements but also with consideration of health and environmental criteria involving airborne toxics and associated health risks, ozone formation potential, hazardous waste generation and surface and groundwater contamination resulting from production, distribution, and use.

To oversee the multimedia evaluation process, the California Environmental Protection Agency (CalEPA) formed a Multimedia Working Group (MMWG) that makes recommendations to the California Environmental Policy Council regarding the acceptability of new fuel formulations that are proposed for use in the State.

The purpose of this document is to set out for both the CalEPA and new fuel applicants a set of recommended guidelines regarding how to approach, conduct, and evaluate a multimedia evaluation.

The key elements of the philosophy and approach in these recommendations are (a) flexibility to address factors unique to each fuel type, and (b) a tiered process for consultation and review using a lifecycle approach. Consultation and review provide a means for the presentation of information by new fuel proponents and feedback iterations from the MMWG aided by expert consultation and peer review. To address the need to provide defensible information and scientific studies that are comprehensive, flexible enough to capture issues unique to each fuel, and based on iterative review and consultation, we recommend a tiered process. In this guidance document we define three tiers during the multimedia assessment process, listed as follows, summarized in Section IV, and each one detailed in Sections V, VI, and VII, respectively.

Tier I: Technical consultation and peer review to establish the risk assessment elements and issues

Tier II: Development and review of experimental design for future actions and reports

Tier III: Implementation of a Final Multimedia Risk Assessment and submission of Final Report that is peer reviewed and is used as the basis for the Multimedia Working Group recommendations that go to the Environmental Policy Council.

The goal of the Tier I review is to develop a mutually-agreed upon Work Plan for the Multimedia Risk Assessment. Tier I begins with the applicant bringing a summary report to the Cal-EPA and ends with an agreed upon Work Plan to proceed through the next two Tiers. The proponent brings to the MMWG a summary of what is known about the properties and hazards of the fuel as best as they can find and based on their experience and expertise. The MMWG establishes the key elements and issues of the decision making process associated with the new fuel. These key elements and issues are peer reviewed. Included in the summary presented to the MMWG are a summary of regulatory approvals, background fuel information, and an outline of information necessary for the Risk Assessment Design to be prepared during Tier II. The goals of the work include the following basic comparative risk assessment and Life Cycle Assessment elements:

1. Physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel and additive components,
2. Summary of all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios,
3. Summary of the expected environmental behavior (transport and fate conceptual models associated with release scenarios) of proposed fuel or fuel components that may be released, and
4. Comparison of physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components.

The final step in the Tier I process is the development and review of the Tier I Work Plan. The Tier I Work Plan is developed with input and concurrence from the MMWG and focuses on key issues that must be addressed in the later Tiers. The applicant must propose the Tier I Work Plan elements and justify the proposed approach to the MMWG for approval. This Work Plan serves to define the issues of the Risk Assessment Design that is carried out in Tier II.

The next step in the multimedia evaluation process is the development and review of the Tier II Risk Assessment Design. The experimental design for final risk assessment work is developed by the applicant and reviewed by the MMWG. The applicant must propose the Risk Assessment Design elements and justify the proposed approach to the MMWG for approval. The Risk Assessment Design should also be peer reviewed.

The Risk Assessment Design should provide a comparison between the proposed fuel or additive and the appropriate California Air Resources Board fuel base fuel. Experimental Design elements address the scope of the risk assessment, and fill any knowledge gaps that are identified in the Tier-I Work Plan including the:

- Role and use of models and surrogate chemicals,
- Manner that used to address health and environmental impacts where experimental tools not well defined, and
- Methodology for integrating all media (air, water, soil, etc.) analysis.

Tier II concludes with a Risk Assessment Design report that addresses all the elements identified in the Tier I Work Plan. It should address the knowledge gaps identified during both the Tier I and Tier II efforts. The final product of Tier II is a Risk Assessment Design report that will be reviewed by the MMWG and peer reviewed prior to execution during Tier III.

The final Tier III Multimedia Risk Assessment submittal should include a summary of preliminary review and experimental design review steps taken through Tiers I and II. The final Multimedia Risk Assessment should also include an expanded analysis of the release scenarios that pose the greatest threat to human health, the environment, and beneficial use of California resources.

The final step in the multimedia evaluation is the completion and review of the Tier III Multimedia Risk Assessment according to the agreed upon design developed through Tiers I and II. A final report is produced that is used as the basis for the recommendations by the MMWG that go to the Environmental Policy Council. This final product, as well as the MMWG recommendations, is also peer reviewed.

II. Introduction

As required by Section 43830.8 California Health and Safety Code, before adopting new fuel specifications the California Air Resources Board (CARB) is required to prepare a "multimedia" evaluation and submit it to the California Environmental Policy Council for final review and approval. In general, the State of California needs information that will allow an informed decision as to the relative risk posed by any newly proposed fuel to the State's resources, human health and the environment. New fuels or potential additives must be evaluated not only with regard to engine performance and emission requirements but also with consideration of health and environmental criteria involving airborne toxics and associated health risks, ozone formation potential, hazardous waste generation and surface and groundwater contamination resulting from production, distribution, and use.

To oversee the multimedia evaluation process, the California Environmental Protection Agency (CalEPA) formed a Multimedia Working Group (MMWG) that makes recommendations to the California Environmental Policy Council regarding the acceptability of new fuel formulations that are proposed for use in the State.

The purpose of this document is to set out for both the CalEPA and new fuel applicants a set of recommended guidelines regarding how to approach, conduct, and evaluate a multimedia evaluation.

III. Philosophy of Multimedia Guidance Document

The recommendations contained within this report have been established through a set of meetings between the University of California and the MMWG. Through this process, a philosophy to interpret and harmonize the recommendations has developed. This philosophy is largely based on lessons learned from other fuel review efforts—in particular with ethanol and PuriNO$_X$. In this section we describe this philosophy. The key elements of the philosophy and approach in these recommendations are (a) flexibility to address factors unique to each fuel type, (b) a tiered process for consultation and review using a lifecycle approach.

A. Flexibility to Address Factors Unique to Each Fuel Type

Each proposed fuel formulation brought to CalEPA for consideration will likely present unique issues that are difficult to fully anticipate in detailed highly prescriptive guidelines. Examples include custom aspects of product or additive manufacture, transport, mixing, and on-site storage requirements; particulars of non-uniform and/or partial market targeting; or potential co-requisite equipment modifications. The multimedia process must also be applicable to emerging transportation fuels of the future such as hydrogen or fuels not yet envisioned. To effectively address such a wide spectrum of possible issues requires guidelines that are both clear about what information is needed in general and sufficiently flexible to adapt to a broad range of fuel formulations and manufacturing/marketing and strategies.

B. Consultation and Review

Consultation and review provide a means for presentation of information by new fuel proponents and feedback iterations from the MMWG aided by expert consultation and peer review. In particular, within the context of a tiered structure, consultation and review provides a mechanism for comments to be given to applicants at intermediate stages of the application process, rather than solely at the end. Because the application process involves a complex and potentially expensive set of activities, providing intermediate review of the decisions made in the design of the multimedia evaluation can save time and effort for all parties involved, and can allow applicants to focus on key issues and uncertainties during the multimedia assessment.

C. The Tiered Approach

To address the need to provide defensible information and scientific studies that are comprehensive, flexible enough to capture issues unique to each fuel, and based on iterative review and consultation, we recommend a tiered process. In this guidance document we define three tiers during the multimedia assessment process, listed as follows, summarized in Section IV, and each one detailed in Sections V, VI, and VII, respectively.

Tier I: Technical consultation and peer review to establish the risk assessment elements and issues.

Tier II: Development and review of Multimedia Risk Assessment Experimental Design.

Tier III: Multimedia Risk Assessment Submittal, Review and Recommendations.

D. Key Assumptions and Benefits of the Tiered Approach

There are several assumptions that support the use of a tiered approach. These assumptions are based upon past experience evaluating new fuels for California. The key assumptions include:

- Each fuel will have some unique features, both in terms of chemistry and potential impacts, and that case-specific guidance can help focus effort and resources for individual applicants. Without early feedback, a proponent runs a high risk of performing unacceptable or unnecessary work.
- Not all the information will be readily available and new fuel proponents will likely need to do additional testing. The proponent will not always have the skilled staff to properly do the additional testing and may need assistance to direct a third party to do the testing.
- The additional testing may be cost prohibitive from the proponents' view and the proponent will want to know how much needs to be done in order to make a decision to proceed.
- There is a value in ongoing peer review of the overall process.

Experience to date supports these assumptions and provides evidence for the inherent benefits of the tiered approach. The benefits to a tiered approach include:

- The key issues and uncertainties associated with a new fuel are identified early so efforts to address these concerns are focused.
- A new fuel proponent can better gauge "when to hold'em and when to fold'em" during the overall process.
- Peer review is ongoing so the overall process has few surprises at the end for either the State or the new fuel proponent.

IV. Background for California's New Transportation Fuel Evaluation Process

In this section we summarize the multimedia evaluation process and the California regulatory review requirements for new transportation fuels including the proposed tiered approach. Detailed guidelines for addressing the goals and targets for each tier are given in the three sections that deal with each tier respectively.

A. An Introduction to "Multimedia" Risk Assessment and Key Elements

In the late-1950s, scientists began to recognize that certain chemical pollutants were capable of persisting in the environment, migrating between air, water, soils and sediments, and accumulating to levels that could harm wildlife and humans. Prior to this time the field of contaminant fate and exposure assessment was concentrated piecemeal on assessing chemical behavior in air, water, or soil as separate compartments, but this paradigm ran counter to the emerging realizations about the behavior of chemicals in the environment. A novel approach was required that described interactions between the seemingly distinct components of the environment – the atmosphere, hydrosphere, lithosphere and biosphere. Since 1985 an entire discipline for multimedia assessment of environmental contaminants has evolved and many useful techniques and modeling tools have been developed. Multimedia fate models are now widely applied for many types of environmental assessments.

A risk assessment is a systematic evaluation of the probability of harm (human disease or ecosystem damage). The elements of a risk assessment include hazard identification, exposure assessment, toxicity assessment, and risk characterization. Hazard identification is used to establish the possibility of harm through toxicological testing that indicates the likely toxic effects of a substance—cancer, reproductive damage, neurotoxicity, etc. The possibility of harm can also be assessed through studies that identify exposure potential based on chemical properties. For example, persistence and bioaccumulation potential are properties of a chemical that increase its likelihood of having a relatively high exposure potential for both humans and ecosystems. An exposure assessment involves source/emission characterization, environmental transport and transformation, and estimates of uptake or intake for humans or other biological organisms. A toxicity assessment is used to characterize the likelihood of harm at a given dose and typically results in a dose-response model. The risk characterization is the process of organizing this information into an estimate of the expected level of harm as well as the reliability (that is uncertainty and variability) in this estimate.

A key element in the development of the risk assessment issues is a conceptual model regarding the behavior of the proposed fuel components in the environment. A conceptual model is a group of hypotheses that summarize expected environmental behavior (transport and fate) of proposed fuel or fuel components. These hypotheses should be supported by literature citations and field data as much as possible. The uncertainty in the data supporting a release scenario conceptual model will be very important in identifying any additional work or research that will need to be performed and each piece of data that needs to be provided to answer a specific question.

A key element in the development of risk management options is the appropriate comparison of physical, chemical, and toxic properties of the proposed new fuel or additive components to an appropriate agreed upon control fuel or fuel components. Generally this comparison fuel will be one that already is widely in use. Existing risk management options may already be in place that are appropriate for the proposed new fuel or additional controls may need to be considered.

The comparative evaluation of new and existing fuel formulations must provide information that can be used to compare relative impacts at different stages of the fuel life cycle (formulation, transport, storage, use) to existing transportation fuels already widely in use. One widely used approach for such comparative studies is Life-Cycle Assessment (LCA). The goal of LCA is to collect relevant information about health and environmental impact for the whole life cycle of a product, from the production of the raw materials to the ultimate disposal of the product. LCA is commonly described as a four step process that includes (1) goal definition and scoping, (2) inventory analysis, (3) impact assessment, and (4) interpretation and improvement. As interest in LCA has increased, a literature and discipline has grown in the area of life-cycle impact assessment (LCIA) (ISO 14042) (ISO 2000, Udo de Haes et al. 2002; Bare et al. 1999, 2000; Udo de Haes et al. 1999a, 1999b; Owens 1997). An important consideration of LCIA is the categories as well as the temporal and spatial dimensions of potential impacts. With infinite time and resources, an LCIA could collect and use extensive amounts of data to incorporate and fully characterize all categories of potential impact and account for all life-cycle stages. But in reality there are time and budget restraints that require the LCIA to restrict its scope to the most important aspects of a particular issue. As a result one of the key goals of LCIA and the proposed tiered multimedia approach is to select the appropriate boundaries, scale, and level of detail required in addressing a specific issue such as fuel formulation. In combination with a tiered strategy, we find that LCA and LCIA approaches are well-suited to address the comparison of different fuel formulations in California.

B. Summary of the Three Tiers of the Multimedia Risk Assessment Evaluation

The multimedia risk assessment evaluation includes three components or tiers each designed to provide input to the next stage of the decision-making process. This process is summarized in Table 1 and illustrated in Figure 1. The process begins with an applicant screening stage. This is a preliminary review by the Cal-EPA MMWG to assess the proposed fuel plausibility and/or feasibility. The purpose of this tier is screen out any proposals that are not worth pursuing even to Tier I. For example, ideas that clearly violate basic concepts of scientific feasibility—mass balance, the laws of thermodynamics, etc., or ideas that appear to be the work of a team with no financial or technical resources to move forward on the concept. The screening review can take as little as few days and should take no longer than a couple of weeks.

Once a project has cleared the screening review, it moves in sequence through the next three Tiers. Tier I begins with the applicant bring a summary report on the fuel to Cal-EPA and ends with either the development of a Work Plan for the Multimedia evaluation or a decision to withdraw the fuel development plan. Tier II follows the Work Plan developed during Tier I to draft a Risk Assessment Design report. During Tier III the Risk Assessment

Design is executed and a report prepared providing the results of the executed Multimedia Risk Assessment.

Table 1. Summary of the recommended Multimedia Risk Assessment process.

<table>
<tr><th></th><th>Fuel Applicant</th><th>Multimedia Work Group</th><th>Peer Review</th></tr>
<tr><td rowspan="2">Tier I</td><td>Fuel Background Summary report:
• Chemistry
• Release Scenarios
• Environmental behavior</td><td>Screens applicant and establishes key risk assessment elements and issues</td><td rowspan="2">Technical consultation during development of Tier I Work Plan including identification of key risk assessment elements and issues</td></tr>
<tr><td colspan="2">Mutually-agreed upon Tier I Work Plan to proceed through multimedia evaluation</td></tr>
<tr><td>Tier II</td><td>Risk Assessment Design report</td><td>Comment on Risk Assessment Design</td><td>Technical peer review consultation of Risk Assessment Design</td></tr>
<tr><td>Tier III</td><td>Execution of Risk Assessment and preparation of Multimedia Risk Assessment report</td><td>Prepare recommendations to the Environmental Policy Council based on Multimedia Risk Assessment report</td><td>Independent peer review of Multimedia Risk Assessment report and Working Group recommendations</td></tr>
</table>

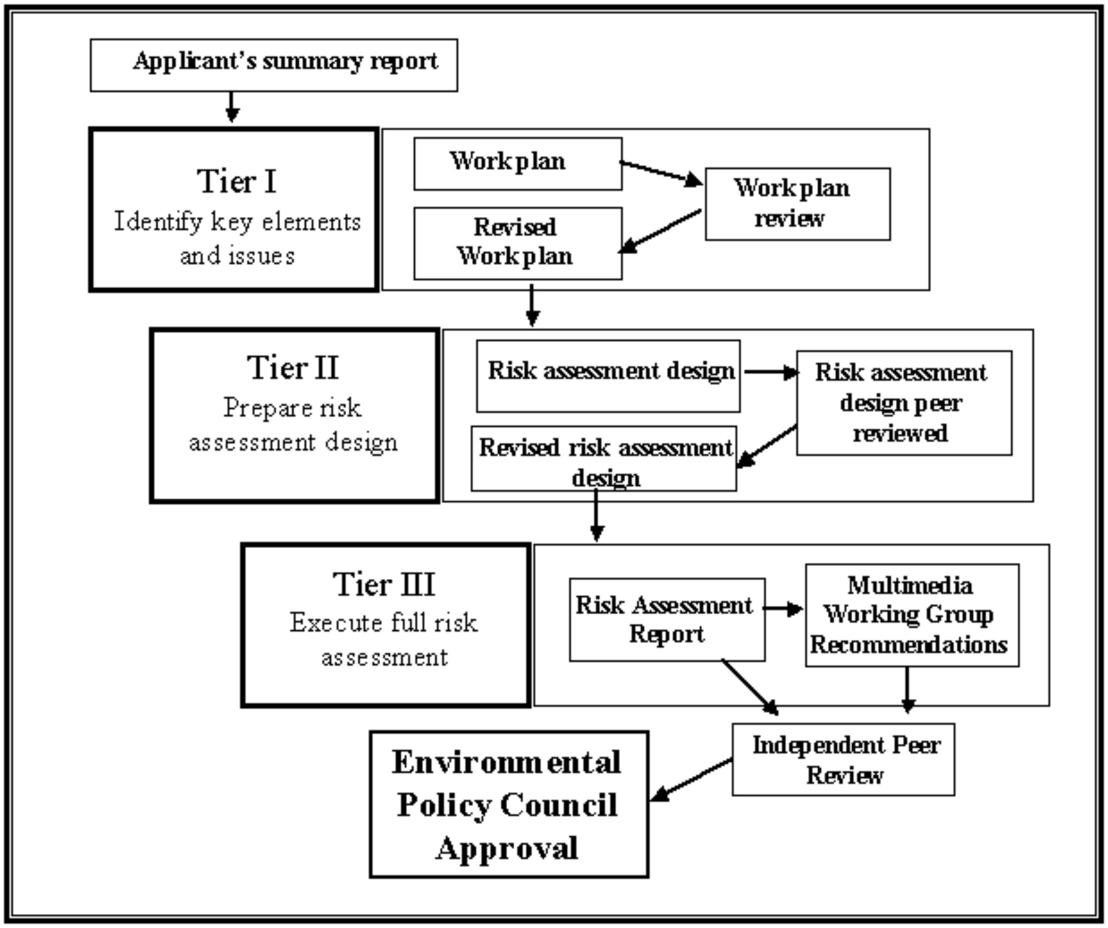

Figure 1 Multimedia evaluation process flow chart

Tier I - Technical Consultation and Peer Review to Establish the Risk Assessment Elements and Issues

The goal of the Tier I review is to develop a mutually-agreed upon Work Plan for the Multimedia Risk Assessment. Tier I begins with the applicant bringing a summary report to the Cal-EPA MMWG and ends with an agreed upon Work Plan to proceed through the next two Tiers. The proponent brings to the MMWG a summary of what is known about the properties and hazards of the fuel as best as they can find and based on their experience and expertise. The MMWG establishes the key elements and issues of the decision making process associated with the new fuel. These key elements and issues are peer reviewed. Included in the summary presented to the MMWG are a summary of regulatory approvals, background fuel information, and an outline of information necessary for Risk Assessment Design. The goals of the work include the following basic comparative risk assessment and LCA elements:

1. Physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel and additive components,

2. Summary of all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios and any waste that may be generated,
3. Summary of the expected environmental behavior (transport and fate conceptual models associated with release scenarios) of proposed fuel or fuel components that may be released, and
4. Comparison of physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components.

The final step in the Tier I process is the development and review of the Tier I Work Plan. The Work Plan is developed by the applicant with input and concurrence from the MMWG and focuses on key issues that must be addressed in the later Tiers. The applicant must propose the Work Plan elements and justify the proposed approach to the MMWG for approval. This Work Plan serves to define the issues of the Risk Assessment Design that is carried out in Tier II.

An expanded description of the Tier I process and initial application requirements can be found in Section V of this document.

Tier II - Multimedia Risk Assessment Experimental Design Review

The next step in the multimedia evaluation process is the development and review of the Risk Assessment Design. The experimental design for final risk assessment work is developed and reviewed by the MMWG. The applicant must propose the Risk Assessment Design elements and justify the proposed approach to the MMWG for approval. The Risk Assessment Design should also undergo technical consultation peer review.

The Risk Assessment Design should provide a comparison between the proposed fuel or additive and the appropriate CARB fuel base fuel. Experimental Design elements address the scope of the risk assessment, and fill any knowledge gaps that are identified in the Tier I Work Plan including the:

- Role and use of models and surrogate chemicals,
- Manner that used to address health and environmental impacts where experimental tools not well defined, and
- Methodology for integrating all media (air, water, soil, etc.) analysis.

Tier II concludes with a Risk Assessment Design report that addresses all the elements identified in the Tier I Work Plan. It should address the knowledge gaps identified during both the Tier I and Tier II efforts. The Risk Assessment Design report will be reviewed by the MMWG and peer reviewed prior to execution during Tier III.

An expanded description of the Tier II process and a discussion of possible Risk Assessment Design elements can be found in Section V of this document.

Tier III - Multimedia Risk Assessment Submittal, Review and Recommendations

The Tier III Multimedia Risk Assessment submittal by the applicant should include a summary of preliminary review and experimental design review steps taken through Tiers I and II. The Multimedia Risk Assessment should also include an expanded analysis of the release scenarios that pose the greatest threat to human health, the environment, and beneficial use of California resources.

The MMWG evaluation of the Multimedia Risk Assessment includes development of recommendations to the Environmental Policy Council. The Multimedia Risk Assessment and MMWG recommendations are then peer reviewed and submitted to the Environmental Policy Council.

An expanded description of the Tier III process and the submittal of the final Multimedia Risk Assessment Report, the subsequent development and peer review of recommendations to the California Environmental Policy Council can be found in Section VII of this document.

C. Summary of Previous Regulatory Approvals and Relevant State Regulations

As part of the preparation for the Multimedia Risk Assessment application at Tier I, the applicant should provide a summary of prior regulatory approvals. This should include any individual state, national, or other-national regulatory approvals that are available or in progress and any government-adopted health criteria, and these approvals should be couched within the context of the relevant California regulations. An example listing of the relevant California regulations are summarized as follows. This catalogue is a static and non-prioritized "snapshot" of the regulatory structure as of early 2006 and is not intended to replace the applicants' research and identification of the proper and up-to-date regulations relevant to their application.

Appendix A provides a list of websites pertaining to regulations and codes applicable to production, distribution and sale of new and alternative fuels in the state of California. The codes also describe the responsibilities of a fuel distributor, and outline the fees and penalties for contamination caused by spills and leakages of fuel products.

The codes linked in Appendix A are each found via the California Environmental Protection Agency's (CalEPA) home webpage, and via the laws and regulations page, on which appear links to laws overseen by different agencies of the CalEPA MMWG. Each of these links leads to a list of links that provides access to each specific law. Provided below is a very brief summary of some highlights of the relevant codes. The applicant is responsible for identification of the most recent and applicable codes at the time of application.

California EPA applicable regulations derive from the Safe Drinking Water and Toxic Control Act of 1986 and enforcement of these codes is discussed in this Act. Also dealt with in this Act is the preservation of rights, referring to the fact that the Safe Drinking Water and Toxic Control act of 1986 can not diminish or alter previously existing codes, regulations or statutes.

Codes and regulations overseen by the Air Resources Board (ARB) that relate to air quality impacts of new and alternative fuels include:

- The California Reformulated Gasoline Regulations. This set of regulations is broken up into two parts. The first part contains codes for vehicle fuel and gasoline that were "sunsetted February 29, 1996." As such, these regulations are no longer applicable. The second part contains two sets of regulations. The regulations that are applicable today are the ones instituted on December 31, 2002 (Phase 3, CaRFG).

- The California Diesel Fuel Regulations. This set of regulations specifies the standards for diesel fuel. The regulations dictate allowable levels of sulfur and aromatic hydrocarbons associated with diesel fuel use in the state. Also outlined in the Diesel Fuel Regulations is the Airborne Toxic Control Measure, designed to reduce particulate emissions from diesel fueled engines.
- Specifications for Alternative Fuels. Contained in this set of specifications are definitions and standards that detail what is classified as an alternative fuel.
- Climate Change Emission Control Regulations. This fact sheet gives information on the current and near future regulations for emissions of "greenhouse gases." Also outlined in this fact sheet are estimated consumer costs.

The Office of Environmental Health Hazard Assessment's (OEHHA) web page lists articles describing applicable codes. The codes and regulations overseen by OEHHA also contain regulations deriving from the Proposition 65 Amendment (1986 and subsequent) to the Safe Drinking Water and Toxic Enforcement Act (1986), and include:

1. <u>Interagency Consultation</u>. This section requires for an inter-agency consultation for anything that might alter the states water quality control standards and or measures.
2. <u>Groundwater Control Programs</u>. The State Water Resources Control Board (SWRCB) is allowed to develop and implement programs designed to protect groundwater quality. Nothing in this section is designed to expand the power of the SWRCB beyond provisions contained in the California Water Code.
3. <u>Discharge of Waste</u>. Waste Policies and definitions are laid out for materials considered hazardous waste. A regional board, in a water quality control plan or in waste discharge requirements, may specify certain conditions or areas where the discharge of waste, or certain types of waste, will not be permitted. Discharge of Oil or Petroleum details regulations and punishments for violating outlined regulations. Also included is a special section about MTBE. Cleanup and Abatement: details regulations regarding cleanup time frames, and applicable monetary punishments for spills and contamination.

The Department of Toxic Substances Control (DTSC)'s is the State agency responsible for enforcing hazardous waste laws. Hazardous waste regulations appear in Title 22 (Social Security), Division 4.5 and are listed on the departmental web page (see Appendix A). The DTSC also adopts emergency regulations when it determines, and the Office of Administrative Law concurs, that there is an immediate need for a regulation to protect the public health and safety, or the general welfare. Typically, emergency regulations stay in effect for 120 days, during which DTSC conducts their rule-making process to permanently adopt the regulations.

The State Water Resources Control Board's mission is he State Board's mission is to preserve, enhance and restore the quality of California's water resources, and ensure their proper allocation and efficient use for the benefit of present and future generations. The codes and regulations overseen by the SWRCB deal with various sections of the California Water Code, and relevant regulations incllude the Federal Clean Water Act (Title 33, U.S.C. sections 1251 and following), the California Code of Regulations, and the Porter-Cologne Water Quality Control Act - (California Water Code, Division 7. Water Quality) with amendments effective January 1, 2006. In light of dramatic regional differences in climate, topography, geology and hydrology, the state is represented by nine Regional Water Quality Control Boards (Regional Boards), whose mission is to develop and enforce water quality objectives and implementation plans which will best protect the beneficial uses of the State's waters.

V. Tier I: Establish Fuel Risk Assessment Elements and Issues

Tier I begins when the applicant brings a summary report to the MMWG and ends with a Work Plan for the Multimedia Risk Assessment design (Tier II) and execution (Tier III).

This section describes the information that a new fuel proponent should bring to the MMWG to begin discussions that will lead to a design of a risk assessment for assessing the multimedia impacts of a new fuel formulation. There is emphasis both on the type of information needed and how this information fits into the tiers that have been identified. At Tier I, the goal is not to answer all the questions, but instead to identify what questions must be addressed and to develop a Work Plan for the types of experiments, models, and evaluations that are needed to confront identified issues. The paragraphs below have been organized to show the information gathering activities according to both process and elements. This information gathering process must be built around a technical peer-review consultation in which the applicant provides preliminary information to the MMWG. The applicant then proposes and justifies to the MMWG a set of key issues and elements that will be used as a basis for the Multimedia Risk Assessment Design. The MMWG accepts or amends this list of key issues or elements aided by expert peer review consultation. The results of this process are described in a Work Plan that is developed by the applicant and endorsed by the MMWG.

Guidelines for preliminary planning and assessment for addressing fundamental risk assessment targets are, restated as follows:

- Physical, and chemical and environmental toxicity characteristics of the reference fuel, candidate fuel and additive components,
- Summary of all potential production, distribution, storage, and use release scenarios including a discussion of the most likely release scenarios and any waste generated,
- Summary of the expected environmental behavior (development of transport and fate conceptual models associated with release scenarios) of proposed fuel, fuel components, or waste that may be released, and
- Comparison of physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components.

A. Technical Peer Review Consultation

The technical peer review consultation begins when the applicant brings to the MMWG a summary of what is known based on their experience and expertise, and available data. It is important that the applicant makes a "good faith" effort to provide complete and useful information. The information provided should include physical, chemical and toxicity properties, release scenarios, and estimates of exposure potential, including:

- Background, reference, candidate fuel information

- Fuel and fuel modifications
- Chemical composition
- Summary of manufacture, transportation and storage of the fuel and additive components
- Historical use of fuel components or additives

Physical, Chemical, and Toxic Properties

In the report that provides a first-tier information for the MMWG and serves as the focus of the technical discussion and consultation, the applicant must provide physical, chemical, and toxic properties data for the reference fuel, the candidate fuel, and individual components (additives) in the proposed fuel. The relevant physical properties of the substance include its physical state at room temperature (solid, liquid, gas);

- physical appearance and color; melting point;
- boiling point;
- density; and
- diffusion coefficients in air or water (if available).

The relevant chemical properties include:

- vapor pressure;
- water solubility;
- octanol-water partition coefficient;
- octanol-air partition coefficient (if available);
- any measure of dissociation in water;
- Henry's law constant,
- any measures of compatibility with conventional storage/distribution materials, and
- any measures of transformation rates in air, water, or soil.

The relevant toxicity properties include:

- any cell tests for mutagenicity (or other cellular-scale measures of toxicity),
- any animal studies of acute LD50,
- a summary of all animal studies of acute toxicity,
- a summary of all animal studies for chronic toxicity.

In addressing the substance properties above, the applicant should consider both the availability and reliability of studies used to establish these properties. Where there are clear gaps, the applicant should propose methods for estimating these properties or experiments to measure the missing properties. Absence of information should not be equated with absence of harm. It is important for the MMWG to have a process for classifying substances with little or no toxicity data. They should not be treated as harmless if there are no data to support or refute the premise that the substances are toxic. Similarly, in the absence of measured chemical (or physical) properties, the applicant may use property estimation methods but all parties must recognize, accommodate and communicate the greater uncertainty introduced to property values obtained from estimation methods rather than measurements.

An important aspect of the applicant's review of substance properties is an effort to assign measures of importance to all information—both available and missing information. To achieve this, the applicant should establish the link among substance properties, release scenarios, exposure pathways and potential ecological or human health risk. The elements of the risk assessment are designed to address specific questions. Thus it is important to identify which substance information (whether available or not) relates to which questions. The applicant should also compare physical, chemical, and toxic properties of the fuel or additive components to appropriate agreed upon control fuel or fuel components

Release Scenarios

During the development of release scenarios a fuel life cycle approach should be used. Release scenarios provide pictures of the various manners that fuel and its components may be released during production, distribution, storage, and use. In considering release scenarios, the applicant should provide a summary of all potential distribution, and use release scenarios as well as a discussion of the most likely release scenarios. From a comparative standpoint, this evaluation provides a means to assess differences between the potential release mechanisms of an existing transportation fuel in wide use and the newly proposed fuel.

Possible release scenarios that should be considered include the following:

- Catastrophic release of fuel or the additive package during pipeline, rail, or truck transport into California. Releases to both freshwater and marine environments, as well as soil and air, should be considered.
- Catastrophic release of fuel or additive package from an underground storage tank.
- Slow release of the modified fuel or additive package from an underground storage tank should also be considered.
- Release of fuel or additive package from a bulk storage container at a production or mixing facility.
- Release during normal use. Worker exposure by dermal or other routes during fuel transfer from or to tanks, changing hoses, etc., should be explicitly considered.
- Air Releases of Criteria Pollutants, Green House Gases, Toxic Air Contaminants, and Ozone Precursors, including exhaust emissions, evaporative emissions, and other emissions that may result from manufacturing, production, transport or accidental releases.
- Additional release scenarios as appropriate for fuel or additive and identified by the State of California or peer reviewers.

Release scenarios are dependent on many assumptions and are not intended to be predictive, although additional consideration is warranted for more likely release scenarios and scenarios that have potentially severe consequences. Therefore, the description of the potential environmental release scenarios should include an evaluation of which scenarios pose the greatest threat to human health, the environment, and beneficial use of water resources. This evaluation will also include estimation of the likelihood of occurrence for each scenario and the basis for that estimate.

Development of release scenarios during **production** should consider:

- The specific make-up of the proposed fuel or additive package,
- How the proposed fuel or additive package will be manufactured, blended, transported and stored, and
- The introduction of trace compounds, preservatives, and process impurities.

Development of **distribution and storage** release scenarios should consider:

- The transportation of the bulk fuel via the various alternatives available, e.g., shipping, trucks, pipelines, rail,
- Estimates of volume by each means of conveyance,
- Storage (includes large bulk above ground as well as smaller below ground) means, and
- The compatibility of additive and/or product with storage and distribution materials.

Development of **use** release scenarios should consider:

- The extent of anticipated use,
- Normal vehicle fueling processes, and
- Both combusted and un-combusted tailpipe emissions.

Release scenarios include both normal and off-normal releases. Normal releases would include combustion and vapor emissions during storage and use and small routine spillage. Off-normal releases encompass failures such as transportation crashes and ruptures of containment vessels. The normal and off-normal release scenarios should consider all possible media to which the proposed fuel may be released including air, ground water, surface water, and soils.

If there is a history of previous use of the proposed new fuel components and there have been previous life cycle releases, then the findings from any associated impacts or field studies should be discussed as part of the release scenario development.

Since the developed release scenarios will be used to focus key multimedia impact issues, it is important to include in the discussion of the release scenarios information regarding:

- Possible site characteristics that may be associated with a release,
- Likelihood of a given release occurrence,
- Risk assessment issues for given type of release, and
- Risk management options for that type of release.

Appendix B contains an example listing of potential release scenarios that were developed during the multimedia evaluation of the use of ethanol as a fuel oxygenate in California. The table includes a brief description of each release scenario, likely site characteristics, an estimation of the likelihood of occurrence, risk assessment issues that may be important during the consideration of each scenario, and risk-management options.

Hazardous Waste Management Issues

It is important to identify hazardous waste that may be generated during the proposed fuel's life cycle particularly from fuel production processes and catastrophic release scenarios. It is necessary for the applicants to identify highly probable hazardous waste generation scenarios and identify the expected waste chemical characteristics. As part of the potential hazardous waste evaluation, the scenarios should include:

- A description of any non-petroleum release that may generate hazardous waste,
- Possible classification of hazardous waste generated, and
- Management approach that could be applied to the identified hazardous waste, including chemical analytical methods that would be applicable to the appropriate release media according to hazardous waste regulatory requirements.

A plan that illustrates how the generated hazardous waste will be managed must be submitted for DTSC to review as part of the Multimedia evaluation. The hazardous waste management plan should consider handling, storage, transportation, disposal, treatment, reduction, cleanup and emergency planning. DTSC would prefer that the plan demonstrate that applicant has considered the preferred hazardous waste hierarchy, in descending order, of 1) source reduction, 2) recycling, 3) treatment, and 4) land disposal. The application must explicitly state if there is no hazardous waste generated in all processes and scenarios. Waste management issues that should be considered include:

- How would a release of the modified fuel respond to standard petroleum cleanup technology and strategies? Would the modified fuel be easier or harder to cleanup?
- If a spill occurred, would the contaminated soils be a hazardous waste? If the contaminated soil is a hazardous waste, what is its appropriate management?
- What hazardous waste is generated in the manufacturing process of the components of the additive package or the modified fuel?
- If the additive package or the modified fuel were discarded, would the waste be a Resource Conservation and Recovery Act (RCRA) hazardous waste or a non-RCRA hazardous waste? What would be the appropriate management of the hazardous waste?

Estimates of Exposure Potential

In the first tier, for proposed fuel or fuel components that may be released the applicant should provide estimates of the expected environmental behavior (transport and fate), and ecosystem and human exposure potential. This evaluation will also include an estimation of the likelihood of occurrence for each release scenario and the basis for that estimate. The expected environmental behavior can be obtained using screening-level fate and transport models with chemical properties identified above as inputs. Environmental behavior should be assessed using key release scenarios. Potential for ecosystem behavior can be based on long-term average concentrations in surface water and soil. Potential for human exposure can be based on concentrations in air, soil, surface water, and ground water combined with exposure factors that account for plausible levels of long-term human contact with these media—i.e. 20 m^3 per day of air breathed, 2 L water per day ingested, etc. An important aspect of the estimate of exposure potential is an estimate of the overall environmental persistence of the chemical components of the fuel. Overall environmental persistence has been shown to correlate with exposure potential for multimedia pollutants.

Tier I Calculations: Fuel Life-Cycle Assessment

At Tier I the goal is to systematically include information about the potential effects of harmful emissions and resource demand so that the applicant and Cal-EPA can make judgments about the relative importance of different environmental impacts. At this stage, the comparative evaluation of environmental stressors addresses the needs of decision makers to target the risk assessment elements and issues needed for Tier II and Tier III. As noted above, one widely used approach for such studies is Life-Cycle Assessment (LCA). In particular the life-cycle impact assessment (LCIA) stage within LCA provides a systematic process by which emissions are evaluated and interpreted to identify the most important contributions and assess overall impact. At Tier I, the LCA process should include a list of toxic chemicals released at each stage of the fuel life cycle, including hazardous waste, any measures of toxicity available for these chemicals (LD50, cancer potency, etc.), estimates of the approximate magnitude of release, and identification of the environmental medium likely to receive the release (air, surface water, soil, ground water).

B. Preparation of a Work Plan to Identify and Justify Key Risk Assessment Elements and Issues

Using information and procedures outlined above, the applicant then proposes and justifies to the MMWG a set of key elements that will be used as a basis for the Multimedia Risk Assessment. Among the elements that will be identified in this process are the following:

- Hazard characterization - Name of the harmful agent; chemical formula (or similar structural identification); relevant biological, chemical and physical properties. Properties that make it potentially harmful to humans.
- Toxicity assessment - Summarize all available information on the toxicity of the fuel constituents. Discussion of human, animal, or other evidence of harmful effects. Report on the availability of any quantitative dose-response model.
- Evaluation of the Potential for human and ecological exposure - Describe scenarios for release and estimate the potential quantities of material released. Use screening level multimedia fate and transport models to explore and quantify how the source relates to concentration at the point of exposure.

C. Multimedia Working Group Acceptance or Amendment of the List of Key Risk Elements and Issues

Through the review and consultation process, the MMWG accepts or amends this list of key elements. If the MMWG amends the list of key elements, it will provide a written report to applicant outlining its concerns and providing guidance and which elements need to be added and how they can be addressed.

Once this process is complete, the applicant completes and submits for MMWG approval the Risk Assessment Work Plan.

VI. Tier II: Develop and Review a Multimedia Risk Assessment Experimental Design

Using the Work Plan developed in Tier I, Tier II comprises further data collection and the development of a Risk Assessment experimental design. Tier II concludes with the preparation and review of a Multimedia Risk Assessment Design report. This section presents summary aspects of the design of experiments used to evaluate rates (fate and transport, partitioning to multimedia compartments, bioremediation, exposure, and toxicology) of the governing processes, as well as issues in waste management and life cycle design for comparative risk assessment. The description is intended to serve as guideline and not as an exhaustive description of experimental protocol or of conceptual model construction for the priority processes, for which appropriate technical materials should be consulted.

A. Background to a Fuel Risk Assessment Experimental Design

Comparative Risk Assessment of Release Scenarios

The Risk Assessment Design should be based on the Tier I Work Plan and provide a comparison between the proposed fuel or additive and the baseline fuel that the MMWG has agreed should be the basis for comparison in the Work Plan. Release scenarios of greatest interest will have been identified in the Work Plan based on the likelihood of adverse impact or occurrence. The examination of the critical release scenarios must be included in the proposed overall risk impact experimental design. The conceptual model assumptions regarding potential transport and fate of fuel components of concern will be very important during this process.

Integration – Methodology of Integrating comprehensive media (air, water, soil, etc.) analyses

The multimedia assessment process requires integration of information across different environmental media, different space and time scales, and different types of populations. In contrast to the single-medium paradigm for assessing impact, a multimedia approach, requires the assessor to locate all points of release to the environment; characterize mass-balance relationships (e.g., between sources and sinks in the environment); trace contaminants through the entire environmental system, observing and recording changes in form as they occur; and identify where in this chain of events actions to mitigate or alter actions would be most appropriate.

To assess exposure and risk a multimedia fate assessment is linked to a cumulative multi-pathway exposure assessment. For both human and ecological receptors this requires that we relate contaminant concentrations in multiple environmental media to concentrations in the media with which a target population has contact. For humans this includes personal air, tap water, foods, household dusts, soils, etc.). The potential for harm is assessed either as the average daily intake or uptake rate, or as time-averaged contact concentration.

How will knowledge gaps be addressed?

Uncertainty in the current state of knowledge regarding the modified fuel should be discussed throughout the data package and key uncertainties should be identified. If experimental data is provided, standards, tests, and experiments used to generate this data must be fully described, and discussed along with proper experimental controls. Whenever possible standardized methodologies should be employed.

To address knowledge gaps, it is important to discuss test-data quality and provide an evaluation of overall uncertainty. In discussing test-data quality, the applicant should consider test data quality (data uncertainty, precision and accuracy, and statistical design issues). The evaluation of overall uncertainty should address the contributions to uncertainty from models, test data, surrogate chemicals, and applicability of testing data.

Role and Use of models

To assess the impact of environmental chemical releases to the ambient environment requires source, transport, exposure and risk characterization models. It must be recognized that these models will thus be important tools to support decisions to tolerate, regulate or monitor existing and new chemical uses. In this role, risk characterization models provide prospective analyses of impacts from new chemicals and retrospective analyses of the links between health outcomes and various chemical uses. In using models to support regulation and monitoring policies, decision makers struggle with the question of how likely are they to make unwarranted choices and what are the associated health, economic, and political consequences of those choices. To confront these questions, decision makers rely on modelers to quantify the representativeness (fidelity) and reliability of their model predictions. So to assist the decision makers in this process, the applicants should go beyond just presenting the models used and results of these models. They should also describe their process of selection and model performance evaluation. At a minimum the applicant should describe the questions to be addressed by models, the conceptual model, and summary details of the model application including choices about how simple or complex to make a model in order to address the question at hand.

Multimedia contaminant fate and exposure models have been useful to decision makers because these models provide an appropriate quantitative framework to evaluate our understanding of the complex interactions between chemicals and the environment. The greatest challenge for multimedia models is to provide useful information without creating overwhelming demands for input data and producing outputs that cannot be evaluated. The multimedia modeler must struggle to avoid making a model that has more detail than can be accommodated by existing theory and data while also including sufficient fidelity to the real system to make reliable classifications about the source-to-dose relationships of environmental chemicals. In Section D below, we outline strategies for using multimedia assessments in a life-cycle based comparative risk assessment.

B. Risk Assessment Elements for Human Health Effects, Ecotoxicology, and Environmental Fate and Transport

Human Health Effects

Human health risk assessment usually requires data on acute effects, sub-chronic effects, and chronic effects via all conceivable routes of exposure. Multimedia evaluation of risk in this context should consider all conceivable risks of exposure to additive components, to their possible degradation products, and to their putative metabolites via air, water, soil, and from direct contact with the fuel. While fuel combustion invokes immediate concerns about inhalation of possible toxic substances, we must also consider unconventional routes of exposure due to multimedia partitioning of fuel or additive components. These additional routes include oral ingestion in contaminated water or food, and dermal absorption after contact exposure. Risk assessment of fuel additives should also include consideration of risk from any impurities likely to be present in the additive components at a concentration high enough to involve significant potential for human exposure in any possible exposure scenario.

There is an enormous variation in testing actually required of new chemicals in the U.S.A. mainly depending on which law or statute they are regulated under (the Federal Insecticide Fungicide and Rodenticide Act [FIFRA], US EPA Toxic Substances Control Act [TOSCA], or neither). Such "testing" may range from "toxicology by analogy", that is, non-testing based upon structure-activity arguments, to "lifetime" testing for carcinogens in both sexes of at least two mammalian species. Many international agencies have also developed minimal testing protocols for new chemicals or new formulations that involve substantial possible exposures, and we have been guided in our recommendations by these suggested testing protocols. We will indicate some typical required test protocols, then try to make recommendations as to which tests are essential and which may be discretionary with the relevant agencies on the basis of their judgment.

Organization for Economic Co-operation and Development (OECD) (a consortium of European agencies, the European Economic Community [EC], the World Health Organization [WHO], and the United Nations) guidelines for chemical testing (OECD, 2004) include:

1. Acute oral toxicity
2. Acute dermal toxicity
3. Acute inhalation toxicity
4. Acute dermal irritation
5. Acute eye irritation
6. Skin sensitization
7. Repeated dose 28-day oral toxicity study in rodents
8. Repeated dose 21/28-day dermal toxicity study
9. Rodent oral toxicity: 90-day study
10. Non-rodent oral toxicity: 90-day study
11. Dermal toxicity study: 90-day study
12. Repeated dose inhalation toxicity: 28-day (or 14-day) study

13. Inhalation toxicity: 90-day study
14. Teratogenicity study
15. One-generation reproductive toxicity study
16. Two-generation reproductive toxicity study
17. Toxicokinetics
18. Reproduction/developmental toxicity screening test
19. Neurotoxicity study in rodents
20. Carcinogenicity studies
21. Chronic toxicity studies ("lifetime")
22. Ames test
23. Multiple genetic toxicology tests
24. Spermatotoxicity tests
25. Percutaneous absorption studies
26. Acute dermal irritation study in human volunteers

It seems reasonable to consider the major risks of exposure to additive components or their combustion/degradation products as either chronic, low dose exposure in air or water, or acute high dose contact exposure during a catastrophic release. The former scenario would suggest that minimal appropriate testing of each component in an additive package include tests # 9, 11, 13, 15, 17, 19, 22, and 23: Rodent oral toxicity: 90-day study, Dermal toxicity study: 90-day study, Inhalation toxicity: 90-day study, One-generation reproductive toxicity study, Toxicokinetics, Neurotoxicity study in rodents, Ames test, and multiple genetic toxicology tests. Such testing should be performed on either the individual components of the additive package or the complete additive package (provided that the composition will not change appreciably from batch to batch). Testing should also be performed on the engine emissions after combustion of diesel fuel containing the additive. Combustion emission analysis should be performed for proposed new fuel mixture with and without the additive package so comparative data are obtained for each proposed additive formulation. The rationale for this requirement is that the additive may change the emission characteristics of the base fuel either for the better or for the worse.

The catastrophic release scenario (see Section VI.A. above) would require that minimal appropriate testing of each component in an additive package include tests # 1-6: acute oral toxicity, acute dermal toxicity, acute inhalation toxicity, acute dermal irritation, acute eye irritation, and skin sensitization.

It is critically important that each of these recommended tests be designed in such a manner that each test has adequate statistical power to ensure that apparently negative results are valid. Any test results submitted to the State of California regulatory agencies, or any proposed testing protocols, should contain a power calculation for each test. The calculation should demonstrate that the (proposed) number of replicates performed at each concentration level and that the (predicted) variability of the results allow a scientifically valid conclusion to be drawn about whether or not the substance is toxic at a given concentration. This may require testing animal numbers at each concentration that are in excess of the standard EPA guidelines for some of the recommended tests.

All required testing must be done, in addition, on major long-lived degradation products of the additive components, and on any major impurities in the additive components. Some, or all, of this testing may already have been performed to satisfy requirements of other agencies outside of California, but additional tests may be required to be run prior to allowing these compounds to be used as fuel additives within California.

These recommendations go beyond the standard EPA Tier II testing (see Appendix C), especially with regard to oral and dermal toxicity testing and in vivo neurotoxicity testing, but this is completely appropriate when considering the implications of multimedia exposure rather than exposure solely by inhalation.

Quantitative structure activity relationships (QSARs) have been suggested as a possible substitute for real toxicity data when requisite tests have not been performed. This is not appropriate for proposed diesel fuel additives because there is no scientific validity to this approach of "toxicology by analogy", and there is a lot of data in the literature suggesting that QSARs do not necessarily make accurate predictions of complex biological outcomes like toxicity.

It might seem reasonable to discount any possible incremental carcinogenicity or other toxicity of additive components to new fuel formulation (additives which, after all, will dilute the carcinogenicity or other toxicity of the original fuel constituents). It is ultimately a risk management decision as to how much apparent toxicity, based upon the test results obtained, is acceptable in a new formulation of fuel, as the fuel itself contains many components with known toxicity. However, we must consider that altering the combustion conditions for the diesel fuel may in itself increase the risk. For example, additives that reduce NO_x emissions by lowering the combustion temperature or altering the size of fuel droplets in the combustion zone may give rise to new or additional products of incomplete combustion (PICs), which are likely to be carcinogens, and which may be released to the multimedia environment. Thus, we require side-by-side testing of combustion emissions from the new fuel with and without additive. Chemical characterization of the combustion products will demonstrate any alteration of emission profiles. Quantitative characterization of specific fuel combustion products with and without additive will suggest additional compounds that require toxicity or genotoxicity/carcinogenicity testing on a case-by-case basis for various additive formulations.

Additional Tests

Taste, odor and color of water play a critical role in its acceptability for many purposes, including human consumption, even if the water is not known to contain constituents at levels thought to produce adverse health effects. This fact is reflected in the preparation of Secondary Maximum Contaminant Limits (Secondary MCL's) for a number of constituents. At the national level U.S. EPA promulgates National Secondary Drinking Water Regulations (NSDWRs or secondary standards), which are non-enforceable guidelines regulating contaminants that may cause cosmetic effects (such as skin or tooth discoloration) or aesthetic effects (such as taste, odor, or color) when they are present in drinking water. Methyl tertiary-Butyl Ether (MtBE) represents a prime example of a contaminant whose removal is driven by such aesthetic considerations since its secondary MCL (based on its undesirable odor) is 5 μg/L while its primary MCL (based on its carcinogenic potential) is 13 μg/L. The goal of related tests is to identify the possibility that a reformulated fuel would be more likely than current fuel formulations to threaten the aesthetic quality of water supplies. One way to accomplish this determination would be to mix the reformulated fuel with water until an equilibrium distribution of constituents between the water-fuel mixture is obtained and to withdraw a sample of the water phase. This sample could then be filtered and tested for color and odor using methods 2120B and 2150B, respectively of the Standard Methods for the Examination of Water and Wastewater (American Water Works Association, 2005). Guidelines for these parameters in treated drinking water are ≤15 units of color (as judged by method 2120B) and ≤ 3 threshold units of odor (as judged by method 2150B). Since dissolved concentrations of constituents imparting odor and color to a water sample should not exceed their equilibrium value in contact with pure phase fuel, and because subsequent treatment should lower these concentrations in many cases, these tests should serve only to alert prospective fuel producers to potential problems with respect to these parameters.

Ecotoxicity

Basic concepts and background material for ecotoxicological testing is provided in Appendix D. The testing protocol and important elements within it are summarized here.

For the testing of fuel additives and new fuels in California, we use the OECD strategy (Figure 1 Appendix D) as a template. Tests for both aquatic and terrestrial environments are covered because release scenarios offer the possibility that both of these ecosystems could be exposed. The aquatic environments are categorized into four subgroups, freshwater pelagic, freshwater benthic, marine pelagic, and marine benthic. Although these could be further subdivided into warm and cold water habitats, the overwhelming majority of freshwater and marine habitats in California are cold water. Consequently, he testing is focused on cold water species. We recommend species that are either native to California, or that have a long history of use in testing programs and for which a considerable toxicity database already exists. The tests are selected based on the coverage of both freshwater pelagic and benthic, marine pelagic and benthic, and terrestrial exposure scenarios. Tests are further selected based on three criteria: Practicality, Validity, and Usefulness. Elements of practicality criteria include: reasonableness of the exposure system, appropriate test duration (covering acute, subchronic, and chronic effects), and availability and maintenance of test organisms. The validity of the test procedure refers to reproducibility of the toxicity experiments, and the limitation and control of the sources of error. Lastly the usefulness of the test in diagnosis is reflected in the: geographical and ecological representativeness, the relevance of the exposure route and test conditions, the extrapolation of endpoints from experimental data, the compatibility with state regulations, and the relative sensitivity exhibited in the data. Details on these individual aspects are given in the Appendix D.

Toxicity tests should be performed by first completing a dose-range finding study. The results of these studies should be made available to the regulatory agencies. At the least, the tests should follow the US EPA Office of Pollution Prevention and Toxic Substances (OPPTS) guidelines (US EPA, 1996, Appendix E) that require chemicals be tested up to a maximum dissolved concentration of 1000 ppm in an attempt to establish a LC50 or an EC50. Once the range finding studies have been completed, the LC50 (for acute tests) or EC50 (subchronic and chronic tests) should be estimated using a sufficient number of treatment concentrations, not including the negative control. Utilizing fewer treatment concentrations may not allow an accurate estimation of the LC50 or the No Observed Effects

Concentration (NOEC). Quantitative Structure Activity Relationships should not be used to estimate toxicity.

Additive components

It is possible that un-combusted additive components from new formulations may be present in the exhaust. Data are needed to determine whether un-combusted additive components from new formulation packages exist in the emissions. Multimedia modeling predicts that soil and sediments may be important reservoirs for various constituents of additive packages after airborne releases. Given that other unregulated combustion products from fuels could also end up in surface soils (e.g., polycyclic combustion products), how would the predicted buildup of un-combusted additives in soil *compare* with levels of PAH under various emissions scenarios? Clearly, to address this question, measurements would be needed of specific additives and/or surrogate compounds during an emissions testing protocol. Once emission rate data are available, then the requisite comparisons can be made between the new and baseline fuels. Note: We should probably specify a program of re-analysis of impact after some period of legal use here**.** At a minimum this would be a compilation of “accident or spill” rate, and an analysis of any reported consequences to ascertain whether the initial assumptions were appropriate.

When the additive package components are blended with fuel, the mixture may act similarly to chemically dispersed oil if released to an aquatic environment. In its evaluation of oil spill dispersants, the National Academy of Sciences (NAS 1989) noted that, for those dispersants studied to date, laboratory data demonstrate that in general, the acute toxicity of dispersed and untreated oil are similar. This indicates that for these surface-active agents, there do not appear to be additive or synergistic effects on aquatic organisms upon exposure to the fuel-dispersant mixture. Extrapolating this conclusion to a spill of modified diesel fuel may be appropriate, although we do not have specific data to support such a conclusion at this time. However, the NAS (1989) report also pointed out that chemically-dispersed oil slicks can affect different organisms than oil (fuel) alone. Surfactants and dispersants released in conjunction with fuel hydrocarbons to aquatic environments have the potential to alter the distribution of spilled fuel, and thus alter the group of organisms that may be adversely affected. Fuel-surfactant mixtures can be expected to partition deeper into the water column than fuel released alone, causing relatively greater exposure to organisms in subsurface waters. This suggests that the actual impacts on aquatic species from a spill may well depend on the timing of the spill relative to the reproductive cycle of aquatic species, as eggs and larvae inhabit different regions of the water column at different times of their life cycle. Additionally, the NAS (1989) noted that if a surfactant-fuel spill occurs in shallow waters with poor water circulation, sediment-dwelling organisms may be affected sooner than from a spill of non-dispersed oil.

Ecological pathways to human toxicity

As in the consideration of toxicity to humans, it is important to consider the major risks of exposure to additive components or their combustion/degradation products as either chronic, low dose exposure in air or water, or acute high dose exposure during a catastrophic release. Testing should be performed on the individual components of the additive package and the complete additive package. Testing should also be performed on the engine emissions after combustion of diesel fuel containing the additive. Combustion emission analysis should be performed for the new fuel mixture with and without the additive package so comparative data are obtained for each proposed additive formulation. All required testing must be done, in addition, on major long-lived degradation products of the additive components, and on any major impurities in the additive components. We recognize that some, or all, of this testing may already have been performed to satisfy requirements of other agencies outside of California, but additional tests may be needed prior to allowing these compounds to be used as fuel additives within California. Finally, estimates of toxicity based on quantitative structure activity relationships should not be substituted for toxicity testing.

Additional toxicity tests beyond the standard acute or chronic toxicity testing used in ecological risk analyses should include consider bioaccumulation in ecosystems. Bioaccumulation is the increase in the concentration of a pollutant in the first organism exposed in the environment. Biomagnification is the increase in concentration of the pollutant in organisms in higher trophic levels. Bioaccumulation does not always result in biomagnification. The potential for biomagnification is a function of the mobility of the pollutant, its half-life in the environment, and its solubility in fat (measured by K_{ow}, the octanol-water partitioning coefficient). Compounds with a high mobility, long half-life, and high K_{ow} tend to biomagnify in the environment. Whether a biomagnified compound becomes problematic from a toxicological perspective is a function of its toxicological properties. While many persistent, fat soluble compounds may have low acute toxicity to organisms in the environment, chronic effects including endocrine disrupting effects can be important. Understanding the bioaccumulation and biomagnification potential of these chemicals is critical to a complete evaluation of their potential environmental effects, and also the potential for these compounds to enter the food chain that eventually results in exposure to humans through ingestion.

Compatibility with intended storage and distribution materials.

One particular release mode is distinct by its partial predictability, that is release through incompatibility of additive components or blended fuels with intended storage and distribution materials. These materials include extant surface and subsurface tanks with associated plumbing, as well as novel systems intended as part of the new fuel distribution, such as mixers or holding tanks. Attention should be paid to characterizing the risk of failure of any such extant or proposed materials under exposure to the new product. To some degree chemical incompatibility can be indicated simply by knowledge of relative chemical differences between the reference and new fuels. More sophisticated experimentally-based investigation may be indicated as part of Tier II experimental design. ASTM is reportedly developing standards for certain and specific such testing; in the absence of such standards experimental design is customized and targeted to knowledge gaps identified in Tier I.

Environmental fate and transport.

Assessment of environmental fate and transport begins with establishment of conceptual models for releases of the modified fuel or mixture components into both surface and subsurface waters. This is distinct from atmospheric phase releases that are to be covered separately. Additionally, consideration should be given to fuel transport as a non-aqueous phase liquid and as a vapor phase. In the subsurface, this should include consideration of the processes that occur under saturated and unsaturated groundwater conditions and should consider the interaction of the fuel with the soil matrix. In the following subsections, the conceptual models of the processes that govern the fate and transport of released fuels/components are described, in the order of fuel-phase and solute transport, multiphase partitioning and sorption, and biodegradation. The last subsection lists several important "frequently asked" technical questions that commonly require attention in multimedia assessment.

Fuel phase and aqueous phase fate and transport.

A high-priority concern of accidental releases of fuels/components to the ground surface is contamination of the saturated water that conveys vulnerability to water supplies most quickly. However the magnitude and the timing of the insult to the saturated zone depends in large part on the rates at which the pure source non-aqueous phase liquid (NAPL) enters and migrates in the subsurface, and the rates of partitioning, to the vapor phase by volatilization and to the aqueous phase by dissolution. Partitioning processes are discussed below; in this subsection we focus on the processes of both fuel phase fate and transport and aqueous phase fate and transport with the latter subdivided into unsaturated zone and saturated zone processes.

Fuel phase (or pure component phase) flow and transport in the subsurface refers to the occurrence, transport and distribution of non-aqueous phase liquids (NAPLs) associated with a fuel or fuel component within soils and other natural porous media subsequent to a release. The processes governing NAPL fate and transport in subsurface environments comprise the physics of flow of immiscible fluids (e.g., Bear, 1972, Chapter 9). The physics are more complicated for two-fluid (NAPL and water, NAPL and air, water [aqueous solution] and air) mixtures and even more complex for three-fluid mixtures. However, useful information can be obtained through examination of basic properties of the fluids involved within a reference porous medium, especially in the context of relative assessment. Also, simple column infiltration experiments can be useful for assessment of relative rates of entry and motion of NAPL into partly saturated and fully saturated porous media.

For a given porous medium (soil or aquifer material) the fluid properties governing NAPL fate and transport are: NAPL density, viscosity, and interfacial tension with water and with the solid phase. NAPL with density greater than that of water is called dense NAPL (DNAPL) and that with density less than that of water is called light NAPL (LNAPL). From experience with primarily gasoline and oil spills on ground surfaces and subsequent monitoring it is well known that DNAPLs percolate vertically downward through the unsaturated zone to the water table (top of saturated zone in unconfined aquifers), continuing downward through the saturated zone. Vertical migration ceases when the DNAPL plume reaches a porous medium with pores small enough that the pressures endured by the DNAPL are below the "bubbling pressure" or entry pressure for the DNAPL to penetrate the material. LNAPLs on the other hand, including most fuels, cease vertical migration at the water table where they form a lens. Either case can present serious long-term groundwater contamination scenarios.

The overall mobility of the fluid includes density and viscosity as factors and so comparison of these basic properties can tell relative motility of the overall fluid during entry and infiltration. Long-term effects of the spill event are also highly dependent on the interfacial tensions among the fluids and solid phase present, because these values determine the occurrence of residual phase in the unsaturated and saturated zones, in the forms of distributed blobs or globules of source NAPL occurring effectively as bubbles within otherwise air/water or water saturated material. The interfacial tensions combine through a relation known as Young's equation to determine the microscopic contact angles between the fluid-fluid interfaces and the fluid-solid interface. For instance considering the two-fluid system of water and NAPL in a porous medium, a small contact angle (a sharp angle between the aqueous-NAPL interface and the aqueous-solid interface) corresponds to a relatively strong adhesion tension in the aqueous phase, so that it becomes the dominant wetting phase. In the opposite case, the NAPL would be the wetting phase. This latter case is typical of many fuels, oils and industrial NAPLs. Thus the interfacial tension dictates the wetting phase, that is, the fluid that predominantly wets surfaces at given saturation levels. This wettability controls the volume and surface area of residual NAPL in a given porous medium, that in turn dictate rates of interphase mass transfer (i.e., contamination of ambient groundwater by dissolution, or partitioning to vapor phase by volatility), in the unsaturated case.

Furthermore, wettability considerations explain "hysteresis" observed in transient conditions where infiltration of a NAPL is followed by water-flooding (as in remediation attempts). Specifically, interfacial tension and wettability may differ when a fluid-fluid interface is advancing or receding in a porous medium. This phenomenon can give rise to enhanced entrapment of NAPL "bubbles" in large pores surrounded by smaller pores, for instance, and has been indicated as a major factor in the difficulty in remediation of NAPL contaminated subsurface. For instance addition of surfactants to the aqueous phase has been found to increase the NAPL contact angle, resulting in vertical mobilization of DNAPL bubbles. Consequently knowledge of the interfacial tensions, as well as densities and viscosities and how they differ between proposed and reference fuels is critical to understanding basic fate and transport of NAPL in the subsurface.

In addition to comparison of basic fluid properties under consideration of multiphase flow in porous media, simple vertical column experiments can illuminate relative rates of infiltration and mobility, as well as differences in residual phase (bubbles or lenses). While the elements of design for such column studies is beyond the current scope, some basic concepts common to all such tests are identifiable. The porous media selected should reflect a variety of natural environments likely to be encountered in the State. The scale of the experiments should be large enough to eliminate edge effects and to allow average porous medium properties to control the fate and transport. This constraint translates into the column diameter and length being significantly larger than the "representative elementary volume" of the porous medium. A simple rule is that the diameter of the column should be at least 100 times larger than the largest scale of structure of porous medium. For instance if a coarse sand is utilized (grain size ~0.5 mm) then the column should be 2-3 inches in diameter. Columns should be packed under water while shaking in order to generate as homogeneous a material packing as possible and to eliminate air pockets (unsaturated columns can be drained subsequent to packing). Alternatively columns can be packed in air and then flooded with soluble gases prior to saturation in order to control bubble formation. Conventional quality control measures apply, such as use of replicates, and controls, in all experiments.

Finally it should be recognized that the natural subsurface is not homogeneous and infiltration of NAPL resulting from spills on any scale are likely to be significantly affected by preferential flow, that is flow along structures in the porous medium more amenable to infiltration and flow. While assessment or prediction of the nature of the porous media involved in any particular spill is obviously intractable, any information the applicant can bring to address relative mobility along highly permeable conduits such as gravel zones, fractures, or open conduits associated with soil biota, would be useful.

Dissolved phase transport in subsurface: Unsaturated. Unsaturated flow governs infiltration of water (as a solution) under gravity drainage (downward), under differences in buoyant densities (density differences with ambient water), and under capillary forces that spread water toward less saturated media. These three processes, gravity drainage, density-induced flow, and capillary redistribution, have rates (under a given hydraulic gradient) that will depend on measurable properties of the aqueous solution, in much the same way that the fuel-phase fluid properties dictate NAPL fate and transport in the multiphase case described above. Thus the unsaturated flow problem can be viewed as a two-fluid simplification of the three-fluid problem above, with the aqueous solution (whose properties depend on the concentration of solutes) being the fluid of concern as it is considered the primary vehicle for contaminants to reach the saturated zone and thereby become available to water supply wells. Although the air (or vapor) phase is usually considered the secondary vehicle its role can be significant, especially if the vapor phase develops a high concentration of fuel component such that density effects incur transport. The relative significance of vapor transport is determined in part by the relative magnitudes of the volatility and Henry's Law partitioning coefficients, and the density increase in the vapor phase.

In addition to the aqueous phase fluid properties, the porous medium properties also contribute to the infiltration process, but for a comparative risk assessment the primary concern is the relative effect on the water solution properties of viscosity, interfacial tension (here between water/fuel component solution and air), and density. Chemical solutes present in the aqueous phase can change each of these basic properties with significant outcome for water flow and transport. Comparative risk assessment to some degree can be addressed by computing relative differences in fluid mobilities and capillary pressures within the context of ideal conceptual models for infiltration such as steady-state vertical flow under a unit hydraulic gradient.

Another consideration in unsaturated flow is the effect of capillary forces on residual water content after passage of a moisture plume, and on such transient conditions in general. As described above for the NAPL infiltration process, interfacial tensions among air, water (as solution), and the porous medium solid phases determine the contact angle between the aqueous solution – air interface and the aqueous solution-solid surface; while in the unsaturated aqueous-air case, the water phase is wetting, the degree of wettability may change with solute concentrations such as fuel components.

As in the NAPL infiltration case, column experiments may also prove useful in assessment of relative effects on water infiltration, residual content, and vapor phase concentrations. Experimental study of water redistribution under capillary forces requires multidimensional observations that may be considered to augment evaluation based on fluid properties.

Dissolved phase transport in subsurface: Saturated. Evaluation of aqueous phase transport in the saturated subsurface seeks to address relative rates of motion with a moving water phase. Motion in the saturated zone is generally much more rapid than that in the unsaturated zone, and so risk assessment questions targeting the saturated zone more often have to do with rates of transport to water supply sources that are as much impacted by partitioning and sorption (next section) as by fluid transport. Also remediation strategies and their relative expected performance can be partly addressed by considering saturated zone transport processes. For instance the conventional "pump and treat" technology involves removal of the contaminant by recycling (with treatment) of the saturated aqueous phase. Under a particular hydrogeologic regime, controlled by the hydraulic gradient, the porosity, and the permeability, the ambient velocities are thus properties of the environment, and the dissolved fuel component properties that matter to eventual fate and transport are contribution to solution density, and diffusion coefficient. These contribute to density-driven transport and mass transfer by diffusion, respectively. As in the NAPL case, density-driven transport imparts an additional vertical velocity to the solute plume when the solution density is greater (downward velocity) or lower (upward velocity) than the ambient fluid. Diffusion provides for entrapment of solute in low-permeability materials present either in well-mixed or poorly mixed subsurface environments, and severely compounds pump and treat strategies.

Partitioning and Sorption.

Revised fuel formulations can negatively impact water quality in several different ways. The most direct and obvious possible impact is that new constituents (e.g., fuel additives) that were not present in the reference fuel may accumulate in environmental compartments that provide routes for exposure to these compounds by humans or other receptors at levels expected to be detrimental. A less direct type of potential impact of the reformulated mixture is that it may increase exposure of receptors (humans or aquatic organisms, for example) to hazardous substances that are present in both the reference and reformulated fuels. This second type of effect might arise for three main reasons:

- *Altered partitioning.* Fuel constituents released to the environment will be distributed among several environmental compartments including free-phase product (i.e., nonaqueous phase liquids, NAPLs), dissolved in the aqueous phase, adsorbed to solid phases (e.g., soils or sediments), or the vapor phase. Any change in this distribution caused by the addition (or removal) of particular fuel constituents will result in altered exposure to hazardous compounds. This change is problematic if it increases constituent concentrations in environmental compartments that drive the exposures but may be beneficial if it increases concentrations in compartments which are responsible for producing little or no exposure in the reference fuel case.

- *Displacement of previous contamination*. Hazardous constituents may have accumulated in particular environmental compartments over time (e.g., sediments or soils) because of historical releases of the reference fuel from, for example, an underground fuel storage tank. If constituents in the reformulated fuel can displace the accumulated constituents, a temporary but significant exposure to the hazardous constituents may be created by release of the reformulated fuel.

- *Reduced biodegradation.* Biodegradation of hazardous fuel constituents may be reduced by addition of a new fuel constituent for several reasons including (i) toxicity of the new constituent toward organisms responsible for biodegradation of the hazardous compound(s), (ii) preferential use of the new constituent as a carbon or energy source by degrading populations, suppressing or eliminating degradation of the hazardous constituents, (iii) alteration of the local environment (e.g., redox status) in such a way to block degradation of the hazardous constituent.

Biodegradation.

Basic concepts and background material regarding biodegradation is provided in Appendix F. In this section we provide a brief summary of assessment and measurement methods.

Biodegradation is an important fate process for potential removal of chemical components of revised fuel formulations that enter aquatic, soil or groundwater environments and, consequently, has the potential to substantially reduce exposure of humans and other receptors. The potential for biodegradation is a function of the chemical's structure, the environment into which it is released, and the types of microbial populations present. In addition, release of these components may increase human exposure to reference fuels that would otherwise undergo natural attenuation. The presence of new fuel components may have indirect impacts (e.g., inhibitory or stimulatory effects) on existing contaminants from fuel because the new compounds may compete for electron acceptors (oxygen, nitrate) or because of metabolic interactions (inhibition, toxicity) (see below).

Assessment of biodegradation potential- overview: The requirements for biodegradation testing of new chemicals vary widely among agencies, both in the US and internationally. Many international agencies have published testing protocols for new chemicals and the most extensive set are those published by the OECD (a consortium of European agencies, the European Economic Community, WHO, and the United Nations). Other approaches include those of the EC and the US EPA.

We summarize test protocols, focusing primarily on those recommended by the OECD, and then make recommendations based on this framework. Most of the information included here is derived from publications of the OECD (OECD, 1995) and the ECB (date?).

The approach for biodegradation testing adopted by the OECD is based on three levels of testing that are categorized as follows:

1. Ready biodegradability, or screening;
2. Inherent biodegradability; and
3. Simulation of environmental compartments (e.g. aquatic, soil, sediment).

The potential for formation of potentially persistent intermediate compounds from the metabolism of the target compound must be considered as well, and this occurs at the second level if there is evidence of partial mineralization (defined as conversion of an organic chemical into its mineral constituents, e.g. carbon dioxide).

The ready biodegradability tests include the dissolved organic carbon (DOC) die-away, carbon dioxide evolution, modified MITI, closed bottle, modified OECD screening, and manometric respirometry tests. The inherent biodegradability tests include the modified semi-continuous activated sludge and modified Zahn-Wellens/EMPA tests. The simulation tests defined by OECD include the aerobic sewage treatment tests but must be expanded, for the purposes of our objectives, to include tests for aerobic and anaerobic soils, anaerobic sediments, lake and estuarine waters. All OECD tests are described in detail in OECD (1995) and the relevant material can be found in Appendix F.

These tests vary in their ease of implementation, cost and how representative they are of environmental conditions. Ready biodegradability tests include screening assays using standardized and simplified conditions and microbial inoculants, such as the Biological Oxidation Demand (BOD) test.

Simulation of environmental compartment tests are more "realistic" assays in which removal of chemicals is measured in microcosms (controlled experimental systems) simulating potential environments into which these chemicals may be released (e.g., aerobic microcosms containing soil). In the latter cases, it may not be possible to isolate biodegradation potential independently but instead one may be looking at the effects of multiple environmental fate processes. Also, given that multiple environmental factors (temperature, pH, soil organic matter, presence of other nutrients, and so forth) and biological factors (types and numbers of microorganisms able to degrade the chemical, types of metabolic pathways they possess), it is difficult to extrapolate, with confidence, from one set of experimental conditions to another.

Some of the requirements for an acceptable test demonstrating that a chemical "passes", e.g. shows signs of biodegradability, include the following (OECD, 1995):

- A positive control (using reference chemical known to biodegrade) should indicate substantial removal during the test period.
- A negative control (no chemical) should show no indication of chemical removal (e.g., measured by carbon dioxide production) during test period
- No more than 20% variation in replicates measuring % removal
- At least 10% removal of the test chemical should occur in a 10 day period.

There is more emphasis on aerobic than anaerobic environmental conditions in the approaches considered above and this is problematic for the assessment of new fuels. A common pathway for release into the environmental is leakage of these chemicals from a service station into an environment low in oxygen (often due to previous consumption of the oxygen during biodegradation of the petroleum contaminants). Careful consideration of the particular exposure scenario(s) (e.g., release to groundwater? release to aquatic sediment?) likely to be relevant for a particular chemical is an important part of the third tier of testing.

The types of soils, sediments and surface waters tested in the simulation test should be representative of the environmental conditions where use or release of the chemical will occur. Specific guidelines describing the collection, handling and storage of soil samples, based on the ISO Guidance documents, are provided by OECD (OECD, 1995)

Different types of information obtained from biodegradation tests useful for multimedia assessment include measurements of the potential for biodegradation, how much biodegradation of the chemical occurred in a specified time period, biodegradation rate (half-life), and identification of daughter products. Biodegradation rates, in particular, are useful input parameters to multi-compartment models of contaminant fate and transport.

Major differences between the OECD and the EC approaches include that the mass of chemical produced can also trigger the progression of the chemical into a higher tier of testing, and scientific judgments regarding the biodegradability of a chemical can be used to move a chemical into a higher tier of testing. The issue of permitting scientific judgment on a case by case basis is an important one to include in our guidelines for multimedia assessment, particularly to determine the need for more stringent biodegradation testing (e.g., at a higher tier) of a chemical when deemed appropriate. Finally the EC scheme puts more emphasis on soil and sediment biodegradation tests than does the OECD and this is an important emphasis for our purposes as well because of the high potential for release of new fuel components into soils and aquatic ecosystems.

C. Tier II Life Cycle Comparative Risk

For Tier-I, we recommended the use of a Life-Cycle Assessment (LCA) Process that includes basic information on the likely level of hazard, but at Tier II this process is expanded to include more information on exposure, toxicity, and risk. Information at Tier I includes a list toxic chemicals released at each stage of the fuel life cycle, any measures of toxicity available for these chemicals (LD50, cancer potency, etc.), estimates of the approximate magnitude of release, and identification of the environmental medium likely to receive the release (air, surface water, soil, ground water, etc.). In contrast to this screening approach, at Tier-II the goal is to systematically include information about the potential effects of harmful emissions and resource demand so that the applicant and the MMWG can make a comparative risk assessment for the fuel or fuel additive relative to agreed upon comparison fuel. The LCA approach can be extended to a comparative risk assessment to make these risk calculations. In particular, the life-cycle impact assessment (LCIA) within in LCA provides a systematic process by which emissions are evaluated and interpreted with regard to potential life-cycle health and environmental impacts. Thus LCIA is an important input to the Tier-II analysis and is an important part of evaluating potential release scenarios and identifying those that pose the greatest hazard. A risk calculation based on LCIA methods is outlined below.

A variety of environmental impact indicators and associated indicators have been developed and more continue to be used as LCIA methodology evolves. LCA practitioners and developers around the world continue to explore and improve impact assessment methodology. Further description of life cycle impact assessment methodology, including discussion on what is and is not LCIA, can be found in a report of the Society of Environmental Toxicology and Chemistry (SETAC, 1997). The scope of an LCA typically does not allow for a full-scale site specific risk assessment. But in the European Union and the US EPA there is widespread use of LCIA tools to make comparative risk assessments.

A toxic equivalency potential (TEP) is a heterogeneous LCIA metric that addresses potential impacts from releases of several chemicals into a number of environmental compartments (Hertwich et al., 1997, 1998, 2001). TEPs provide transparent representations of actual processes based on primary attributes. These attributes are developed using measured and/or estimated data in models that focus on factors judged to be crucial. The human toxicity potential (HTP) is a quantitative TEP that was introduced by Hertwich et al. (2001) to reflects the potential harm of a unit quantity of chemical released into the environment by including both inherent toxicity and generic source-to-dose relationships. The TEP uses the HTP framework as a starting point.

The SETAC Europe Working Group on Impact Assessments (Hauschild and Pennington, 2000) has proposed three factors to characterize human and ecological effects in LCIA.

These are (1) an emission factor to account for mass loading, (2) a source-to-concentration factor to account for transport and transformation and (3) a toxicity factor to account for harmful effects. With this framework, an LCIA impact score S is presented as the product of three factors:

$$S_i^{mn} = M_i^n F_i^{nm} E_i^m \quad (1)$$

Where M is the total mass loading of the emissions, mol/d; F is a fate factor, mol/m3 per mol/d; and E is an effect factor, damage per mol/m3. The index i represents the chemical, n the environmental compartment to which the emission is released, and m the medium of exposure of the ecosystem or human, air, soil, water, food, etc. In order to obtain the total impact score within an impact category for all emissions in the functional unit, life cycle or life cycle stage, the individual impact scores are summed across chemicals, compartments of release, and media of exposure:

$$S = \sum_{i,m,n} S_i^{nm} \quad (2)$$

Uncertainty and Sensitivity

Confronting the capabilities and limitations of LCIA calculations requires model performance evaluations. This evaluation should estimate the degree of uncertainty in the assessment and illustrate the relative value of increasing model complexity, providing a more explicit representation of uncertainties, or assembling more data through field studies and experimental analysis. Uncertainty in risk assessment predictions arise from a number of sources, including specification of the problem; formulation of the conceptual model, estimation of input values and calculation, interpretation, and documentation of the results. Of these, only uncertainties due to estimation of input values can be quantified in a straightforward manner based on variance propagation techniques. Uncertainties that arise from miss-specification of the problem and model formulation errors can be assessed using tools such as decision trees or based on elicitation of expert opinions (Ragas et al., 1999).

Sensitivity and uncertainty analyses are powerful tools for assessing the performance and reliability of models. As applied to mathematical models, sensitivity analysis is quantification of changes in model outputs as a result of changes in individual model parameters. Uncertainty analysis is the determination of the variation or imprecision in the output function based on the collective variation of the model inputs. A full discussion of sensitivity and uncertainty analysis is provided in the text by Morgan and Henrion (1990) and the volume edited by Saltelli et al (2000). The goal of a sensitivity analysis is to rank input parameters, model algorithms or model assumptions on the basis of their contribution to variance in the model output.

D. Frequently Asked Questions

Beyond the basic processes covered in the previous subsections, fate and transport conceptual model questions that should be addressed include:

- Will there be any changes in tailpipe emissions that could affect water quality (i.e., through washout)?
- What are the effects on capillary and soil pore conditions and partitioning within the soil environment?
- What are the effects on the fate and transport of surface and groundwater plumes – Once it reaches water, will a modified fuel plume move faster or farther or be more persistent than, for example, ultra-low sulfur diesel?
- Will there be any relative change in biodegradation rates? Biodegradation of hazardous fuel constituents may be reduced by addition of a new fuel constituent for several reasons including (i) toxicity of the new constituent toward organisms responsible for biodegradation of the hazardous compound(s), (ii) preferential use of the new constituent as a carbon or energy source by degrading populations, suppressing or eliminating degradation of the hazardous constituents, (iii) alteration of the local environment (e.g., redox status) in such a way to block degradation of the hazardous constituent.
- What will be the ultimate fate of the product by component as compared to existing fuel specifications or for the new components in the modified fuel that are not already in existing fuels (mass balance)?
- Will daughter products be produced during natural environmental transformation processes and what is the hazard associated with these daughter products?
- What will be the impact if a release commingles with existing soil/groundwater contaminated with petroleum hydrocarbons or fuel additives such as MtBE or Tert-Butyl Alcohol (TBA)? Specifically, will the modified fuel mobilize petroleum contaminants in soil or groundwater?

E. Outcomes from Tier II

The end products of Tier II are a Risk Assessment Design report and a Tier II peer review report with MMWG approval. The Tier II peer review report will define the steps needed to revise the Risk Assessment Design that will be executed to prepare a Tier III Multimedia Risk Assessment report.

VII. Tier III: Multimedia Risk Assessment Submittal, Review and Recommendations

During Tier III the products of the Tier II efforts are used by the applicant to prepare a final comparative Multimedia Risk Assessment. A final Multimedia Risk Assessment report is prepared and submitted to the MMWG for evaluation and preparation of recommendations to the Environmental Policy Council. Prior to submittal to the Environmental Policy Council, the submitted Final Multimedia Risk Assessment report as well as the MMWG recommendation will undergo independent external expert Tier III Peer Review.

Due to the level of specificity and uniqueness that will likely be encountered with each newly proposed fuel or fuel component, the guidance offered in this section will focus primarily on the general information and format needed for the Final Report and Tier III Peer Review.

It is anticipated that applicants may be eager to streamline the multimedia evaluation process and may seek to proceed directly to the preparation of the Tier III Final Report, especially if the application process is viewed as redundant with prior applications elsewhere. The evaluation of Tier III application materials however is based on the mutual concurrence between the State and the applicant of the hypotheses, conceptual models, and plans justified in Tiers I and II, that are unique. Therefore, the risk of this strategy may be realized if the MMWG or the Tier III Peer Review Experts find that key analysis have not been performed or uncertainties have not been properly addressed. This could result in expenses during the multimedia process that were unproductive and additional expenses that will be needed to complete the process, including a restart from Tiers II or I.

A. Summary of Tier I and Tier II Results

Since the Multimedia Final Report will be submitted to an independent external peer review panel, the panel will need sufficient information to understand the steps and agreements that have been reached during the movement through Tiers I and II. There should be sections in the Final Report that are devoted to summarizing:

- The basis for selecting the comparison fuel
- Fuel Life Cycle Analysis and release scenario assumptions and conclusions
- Transport and fate conceptual model hypotheses and assumptions
- Exposure pathway and toxicological hypotheses and assumptions
- Key uncertainties that have been identified and the methods and approaches taken to address these issues
- Methodology used during the comparative Multimedia Risk Assessment

B. Findings and Conclusions of the Comparative Multimedia Risk Assessment

In addition to presenting the results of the completed multimedia risk analysis, the findings and conclusions of Final Multimedia Risk Assessment report should include sections that explicitly discuss the following topics:

- Impacts to air resources
- Impacts to water resources
- Impacts to human health
- General environmental impacts
- Waste management issues
- Cost-benefit-tradeoffs

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IX. RECOMMENDATION AUTHORS

TIMOTHY R. GINN - Author and Editor

Professor, Department of Civil and Environmental Engineering, University of California, DavisProf. Ginn's research and teaching is focused on quantitative analyses of environmental systems with abiotic/biotic mixtures, including biogeochemical cycling and risk assessment endpoints. He has studied reactive transport of multiphase, multi-component mixtures with inorganic, organic, and biotic components in natural and engineered environments. His research in quantitative risk assessment includes dose-structured population dynamics and ecotoxicology, inactivation of particle-associated pathogens in wastewater, and experimental design for multimedia risk assessment. His research in quantitative hydrogeology includes multi-component fate and transport in the natural subsurface, bioremediation and bacterial/ colloidal transport in porous media, kinetics of biotic reactions with lags, estimation of groundwater recharge and age, and inverse problems. He has published over 60 articles or book chapters in environmental modeling and hydrogeology.

THOMAS E. McKONE - Author and Editor
Adjunct Professor, School of Public Health, University of California, Berkeley
Senior Scientist, Deputy Department Head, Indoor Environment Department, Lawrence Berkeley National Laboratory, Berkeley CA.

Dr. McKone's research interests include the development, use, and evaluation of models and data for human-health and ecological risk assessments; chemical transport and transformation in the environment; and the health and environmental impacts of energy, industrial, and agricultural systems. He is responsible for the development of CalTOX, a model first used by the California Environmental Protection Agency to conduct multimedia risk assessment for hazardous waste and air pollutants. More recently, CalTOX has been used for assessing the behavior of persistent pollutants and for life-cycle impact assessments. In addition to his research and teaching activities with the University of California, Dr. McKone is active in other research, regulatory, and professional organizations. He has been a member of several National Academy of Sciences Committees and served six years on the EPA Science Advisory Board. He is past-president of the International Society of Exposure Analysis (ISEA) and has been on consultant committees for the Organization for Economic Cooperation and Development (OECD), the World Health Organization, the International Atomic Energy Agency, and the Food and Agriculture Organization. The ISEA awarded him the 2003 Constance L. Mehlman Award for "contributions in exposure analysis research" that have provided "new approaches for the reduction or prevention of exposures" and have "helped shape national and state policies." Dr. McKone is author or co-author on more than 100 papers in peer-reviewed journals.

DAVID W. RICE, JR - Author and Editor
Environmental Scientist, Environmental Restoration Division, Lawrence Livermore National Laboratory, University of California, Livermore, California.

Mr. Rice is an expert on the fate and transport of contaminants in subsurface sediments, ground water, and the marine environment. He directed the preparation of the assessment of the environmental impacts of the use of ethanol as a fuel oxygenate in California and was the Project Director for the evaluation of multimedia impacts resulting from the use of PuriNOx fuel in California. He has directed the Chlorinated Volatile Organic Compound (CVOC) Historical Case Analysis Study, the Department of Defense Petroleum Hydrocarbon Cleanup Demonstration Program and was the lead scientist for a team of University of California collaborators assisting the State of California in re-evaluating leaking underground fuel tank cleanup decision-making processes. During his 30 years at Lawrence Livermore National Laboratory (LLNL), Mr. Rice has participated in the management of the LLNL superfund sites and directed and performed research on environmental decision-making, information management, and decision support systems for the optimization of environmental remediation. His research includes the application of risk-informed decision-making to environmental restoration activities, the life cycle environmental impacts of fuel choices, and cost/benefit analysis and multiple stakeholders interactions during environmental decision making. Mr. Rice has authored/co-authored over 60 publications.

MICHAEL L. JOHNSON - Author
Associate Research Ecologist, John Muir Institute of the Environment, University of California, Davis.

Dr. Johnson is an expert on ecological risk assessment in terrestrial and aquatic environments. He has worked on ecological risk assessments at Mare Island Naval Shipyard and Edwards Air Force Base, both in California. He has served as a reviewer of several ecological risk assessments including Alameda Naval Air Station, and performed the ecological risk assessment analysis for the University of California's assessment of the risk posed by the release of Methyl Tertiary Butyl Ether (MTBE) to the environment. Dr. Johnson also served as a reviewer for the ecological risk assessment portion of the analysis of the potential impacts resulting from the use of PuriNOx fuel in California. He is on the editorial board of the Bulletin of Environmental Contamination and Toxicology and regularly serves as a reviewer for numerous journals on subjects such as ecological risk and chemical contamination of water, soil, and biota. He also served as a member of the expert panel to review scientific studies proposed as benchmarks for toxicity assessments used in the ecological risk assessment at Vandenberg Air Force Base, California. Dr. Johnson was the Director of the Ecotoxicology Lead Campus Program of the University of California Toxic Substances Research & Teaching Program. His past and current teaching responsibilities at the University of California, Davis include Introduction to Environmental Toxicology and a graduate level course in Human and Ecological Risk Assessment. Dr. Johnson's current research involves investigating the exposure and effects of metals and organic compounds on organisms in aquatic ecosystems.

JEROLD A. LAST - Author
Professor in the Division of Pulmonary and Critical Care Medicine, Department of Internal Medicine, School of Medicine, University of California, Davis.

Professor Last served as Director of the Toxic Substances Research and Teaching Program, a University of Californa (UC) System-wide program, for almost 20 years, and is currently Director of an National Institute of Health Fogarty International Center to promote research in environmental toxicology and environmental epidemiology in South America, especially Uruguay, Argentina, and Chile. Previously he was vice-chair of the Department of Internal Medicine at UC Davis and Chair of the Graduate Group in Pharmacology and Toxicology. He chaired an UC System-wide panel that advised the state on policies with regard to MTBE in gasoline. His Ph.D. degree is in Biochemistry. He maintains an active research laboratory that studies mechanisms of pathogenesis of asthma and health effects of air pollutants on the lung, and has authored/co-authored more than 200 publications in technical journals.

KATE M. SCOW - Author
Professor, Department of Land, Air and Water Resources, University of California, Davis.

Professor Scow teaches and conducts research related to environmental microbiology, microbial ecology and contaminant fate and transport in soils and groundwater. Current research activities include remediation and biodegradation of MTBE and perchlorate in the subsurface, impacts of ethanol on natural attenuation of petroleum, and impacts of antibiotics on microbial communities. Prof. Scow is also Director of the Kearney Foundation of Soil Science, an endowed UC program that funds research on soils and water. With academic degrees from Cornell University in Soil Science (M.S., Ph.D), Prof. Scow is broadly interested in understanding and managing microbial processes that contribute to the remediation of contaminants in the environment. Prof. Scow has authored/co-authored over 120 publications in technical journals.

THOMAS M. YOUNG - Author
Associate Professor, Department of Civil & Environmental Engineering, University of California, Davis.

Professor Young teaches and conducts research related to environmental chemistry and contaminant fate and transport. Current research activities include remediation and transport of organic contaminants in the subsurface, multimedia transfer of contaminants, transport and transformation of pesticides, and the impacts of stormwater on surface water quality. Prof. Young worked in the Office of Underground Storage Tanks in the US Environmental Protection Agency and has been involved in technical and policy issues related to prevention and cleanup of underground fuel releases for more than 20 years. With academic degrees in Chemical Engineering (B.S.), Public Policy (M.P.P.) and Environmental Engineering (Ph.D.), Prof. Young is broadly interested in environmental decision making, especially in the quality and utility of the underlying information. Prof. Young has authored/co-authored over 35 publications in technical journals.

X. APPENDICIES

Appendix A: List of websites for regulatory information

Cal EPA homepage: http://www.calepa.ca.gov/

Cal EPA regulations: http://www.calepa.ca.gov/LawsRegs/

ARB regulations: http://www.arb.ca.gov/html/lawsregs.htm

DTSC regulations: http://www.dtsc.ca.gov/LawsRegulationsPolicies/index.html
DTSC fact sheet for hazardous waste generators:
(http://www.dtsc.ca.gov/HazardousWaste/upload/HWM_FS_Generator_Requirements.pdf).

OEHHA regulations: http://www.oehha.org/prop65/law/index.html

WRCB regulations: http://www.swrcb.ca.gov/water_laws/index.html

Appendix B: Example Release Scenarios for the use of ethanol in gasoline (Rice, D.W., S.E. Powers, and P. J.J. Alvarez. 1999. Potential Scenarios for Ethanol-Containing Gasoline Released into Surface and Subsurface Waters. Vol 4, Chapter 1 *in* Health and Environmental Assessment of the Use of Ethanol as a Fuel Oxygenate. Lawrence Livermore National Laboratory. UCRL-AR-135949).

Production:

Release Scenario: AST Release	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options
This scenario assumes a large volume (> 30,000 gallons) bulk ethanol release to soils and ground water at an ethanol-manufacturing site. The release is assumed to be from a high-volume aboveground storage tank (AST) or associated piping.	This scenario assumes bulk ethanol release into relatively pristine subsurface conditions. Fuel hydrocarbons are assumed to be historically absent.	Small likelihood of occurrence. Since California currently has few ethanol production facilities, this scenario represents a release that could occur once biomass ethanol production facilities are constructed in California in the future.	Toxicity to ecological receptors in direct contact with the release. Case studies indicate that ethanol is relatively rapidly degraded in the subsurface environment.	Engineered containment to control potential release, e.g., double walled tanks and piping. Spill prevention and containment contingency (SPCC) Plans typically in place.

Distribution:

Release Scenario: Bulk Ethanol Transport by Rail or Highway	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options
This scenario assumes a rupture of a rail tank car or tanker truck and the release of a large volume of bulk ethanol (10,000 – 30,000 gallons) to soils and ground waters or surface waters.	This scenario assumes a bulk ethanol release into relatively pristine surface and subsurface conditions where fuel hydrocarbons are assumed to be historically absent.	Moderate likelihood of occurrence. Since California currently has few ethanol production facilities, most ethanol used will initially be transported into the state by rail tanker car or truck.	Toxicity to ecological receptors in direct contact with the release. Potential to impact surface aquatic ecosystem. It is likely that volatilization as well as biodegradation will be important mechanisms in the rapid natural attenuation of the bulk ethanol.	Tanker cars and truck releases are typically treated as an emergency response action and generally require no long term monitoring.

Bulk Ethanol Transport by Marine Tanker				
This scenario assumes a rupture of a marine tanker ship and the release of a large volume of bulk ethanol (> 100,000 gallons) to marine surface waters.	This scenario assumes a bulk ethanol release into the near shore coastal marine environment.	Low likelihood of occurrence. The marine shipping of ethanol will increase since distribution hubs will prefer to receive larger quantities and minimize the handling of rail cars.	Toxicity to ecological receptors in direct contact with the release. Potential to impact surface aquatic ecosystem. It is likely that dispersion and dilution as well as biodegradation will be important mechanisms in the rapid natural attenuation of the bulk ethanol.	Require shipment in marine tankers with double wall construction.

Distribution (Continued):

Bulk Ethanol Storage at a Distribution Terminal				
This scenario assumes a large volume bulk ethanol release to soils and ground water at a distribution hub or terminal. The release is assumed to be from a high-volume aboveground storage tank (AST) or associated piping. ASTs at a distribution hub may contain >150,000 barrels of ethanol.	Fuel hydrocarbons are assumed to be historically present and may be present as free product trapped in the subsurface. MTBE may be present in the free product.	Moderate likelihood of occurrence.	The ethanol is assumed to interact with soils contaminated with existing fuel hydrocarbons. Will previously immobile hydrocarbons now be mobilized to the ground water? Will an existing fuel hydrocarbon ground water plume be expanded?	Engineered containment to control release, e.g., double walled tanks and piping. SPCC Plans typically in place. Manage the location of ethanol ASTs to avoid known areas of fuel hydrocarbon releases. Remediate the fuel hydrocarbon releases.

Release Scenario: Blended Gasohol Release During Transport	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options
This release scenario assumes that ethanol is blended with gasoline at a distribution terminal or refinery and transported by tanker truck to a gas station. A large volume (~ 5000 gallons) of blended gasoline/ethanol (10% or 6% gasohol) could be released from tanker truck to soils and ground waters or surface waters.	Releases occur into roadside environments where fuel hydrocarbons are historically absent.	Moderate likelihood of occurrence.		Tanker cars and truck releases are typically treated as an emergency response action and generally require no long term monitoring

Distribution (Continued):

Gas Station Releases

This scenario assumes that gasohol is spilled during underground storage tank filling at a gas station. A low volume (< 50 gallons) of blended gasoline/ethanol (10% or 6% gasohol) could be released to soils and groundwater.	Small masses of fuel hydrocarbons are assumed to be historically present in the subsurface.	A likely and common release scenario.	The ethanol is assumed to interact with soils contaminated with existing fuel hydrocarbons. MTBE may be present.	Underground storage tank over-fill buckets associated with up-graded USTs should minimize these releases.
This scenario assumes a small puncture of the UST or associated piping resulting in a low volume release of blended gasohol (~ < 3 gallons per day).	Releases may occur into subsurface environments with or without historic fuel hydrocarbon contamination.	A likely and common release scenario. Evaluation of this scenario will be important to estimating potential impacts to ground water resources.	This scenario has the potential to release a large cumulative mass of gasohol because of the large number of USTs in operation and the potential for small leaks to go undetected.	Current requirement for USTs to use double wall containment reduce the likelihood of this scenario's occurrence. There remain some issues with materials compatibility with ethanol.
This scenario assumes a large puncture of the UST or associated piping resulting in a high volume release of blended gasohol (~ > 10 gallons per day).	Releases may occur into subsurface environments with or without historic fuel hydrocarbon contamination.	Moderate likelihood of occurrence.	Typically, larger UST leaks are rapidly detected and corrective action is initiated.	Current requirement for USTs to use double wall containment reduce the likelihood of this scenario's occurrence. There remain some issues with materials compatibility with ethanol.

Use:

Release Scenario	Site Characteristics	Likelihood of Occurrence	Risk Assessment Issues	Risk Management Options
Release from watercraft emissions into surface waters.	Pristine freshwater lakes and rivers.	A likely and common release scenario	The biodegradation of ethanol in surface waters is expected to rapid. Low increases in nutrient loading may occur.	
Rainout of tail pipe emissions and combustion products to surface soils and waters.	Wide spread non-point source deposition with various amounts of recharge to ground waters and runoff to surface waters.	A likely and common release scenario.	Henry's Law partitioning calculations will be a good first approximation of the magnitude of the ethanol rainout. The biodegradation of ethanol in surface waters is expected to rapid.	

Appendix C. EPA Guidelines for Human Health Testing

February 10 ,1998

US Submission to Meeting
of OECD Working Party on Existing Chemicals
February, 1999

HPV Chemical Human Health Testing:
Animal Welfare Issues and Approaches

EPA is mounting a very extensive program to obtain toxicological screening information on chemicals of High Production Volume (HPV), that is, substances produced in excess of 1M lb/year. Current information indicates that there are about 2800 chemicals with that designation. Various parties have noted that if each chemical in the program were to be tested for each of the human health effects tests, a large number of animals would be employed. In recognition of these concerns, the Agency has given thought to the issue and is developing a strategy to reduce animal use while still generating needed high quality health information.

Many different paths are being investigated to ensure the minimization of animal usage and optimization of procedures for those animals that go into test in the HPV testing program:

1. Decreasing chemicals going into test

a. Industry will determine whether adequate information on chemicals already exists for the various endpoints. We do not want to retest chemicals.

b. EPA has released a data adequacy document which provides guidance on making such determinations. EPA is also in the process of developing guidance on procedures for searching the literature on other sources of existing information.

c. Both the OECD's HPV Program and the HPV Challenge in the U.S. encourage industry to develop categories of chemicals which can be assessed as a group. These categories of related chemicals are expected to share chemical and biological attributes. Instead of gaining information on all members of a category, attempts will be made to identify testing strategies that will identify individual materials which are representative of the category. By testing the identified individual materials, we should be able to characterize the potential fate and effects of the whole category.

d. Structure-activity relationships (SAR) will help to identify potential toxicities and other effects of individual chemicals based on Quantitative Structure Activity Relationships (QSARs) or "read-across' (i.e., analogue) approaches.

2. Minimizing and optimizing animal use in tests

The HPV testing program includes acquisition of health effects data for chemicals on acute toxicity, reproductive toxicity, developmental toxicity, 28-day repeated dose toxicity and mutagenicity. Mutagenicity data requirements can be fulfilled with bacterial gene mutation, in vitro mammalian cytogenetics (for pre-existing information) and in vivo micronucleus (for pre-existing or newly generated information). Several opportunities are available to evaluate the role of animals in testing and ensure that their use is being appropriately addressed.

a. **Replacement of animal testing**. In some cases we need not obtain health hazard information in animals. Mutagenicity testing can be fulfilled by bacterial systems (e.g., Salmonella gene mutation) and, in some cases, by cytogenetics in cultured mammalian cells.

b. **Refinement of animal testing**. EPA supports the employment of federal and voluntary measures to ensure humane care and upkeep of laboratory animals. In addition, we plan to utilize principles developed in an upcoming document on humane endpoints from OECD. This report will lay out signs of pain and stress in animals that should be utilized in deciding when to terminate animals in test.

c. **Reduction of animal testing**. There are several opportunities to reduce the number of animals committed to test. **Table 1** illustrates potential animal savings for the case where some or all health effects tests are performed on a chemical.

(1) **Acute toxicity**. There are 4 acute oral toxicity tests approved by OECD. In the use of the traditional test (OECD 401), about 30 animals are employed to screen for toxicity following a single exposure. Three alternative methods either refine or reduce animal usage. Data from any of the acute methods may yield appropriate information for HPV testing. Among the three alternative methods, EPA has identified a preference for the up-and-down method (OECD 425) for the following reasons: it greatly reduces the number of animals in comparison to OECD 401 (the up-and-down method uses approximately 8 animals versus 30 in OECD 401); it gives a point estimate of the LD50; and it yields information that can be used to estimate the toxicity of chemical mixtures in accordance with the UN transport classification system.

(2) **Reproductive and developmental toxicity**. There are separate test guidelines for 1-generation reproduction toxicity (OECD 415) and for prenatal developmental toxicity (OECD 414; revision of this test is ongoing at OECD). If separate reproduction and developmental toxicity tests were conducted using current OECD 415 and 414 protocols, 320 animals would be used. To screen for

reproductive and developmental toxicity and to reduce animal usage in comparison to the separate test guidelines, EPA recommends use of a combined toxicity protocol (OECD 421) for the U.S. HPV testing program.

(3) **28-Day repeated dose toxicity**. Instead of conducting a stand-alone 28-day oral toxicity test (OECD 407), the endpoints covered by that guideline can be combined with the reproduction/developmental toxicity screen into OECD 422 with no increase in number of animals over that used in OECD 421.

(4) **Mammalian micronucleus**. The traditional in vivo micronucleus test is performed using 2 sexes and a concurrent positive and negative control. EPA is exploring the idea of using at least the males from OECD 422 for all but the positive control. Females may need to be dosed separately.

(5) **Overall animal savings**. By selecting specific tests, there could be a significant savings in animals committed to test in the HPV program. If the traditional acute, reproduction, developmental and 28-day repeated dose toxicity studies and the in vivo micronucleus test were separately employed, a total of 440 animals might be used. By using alternative and combined test protocols, the number of animals could be reduced to 118, a savings of 322 animals (>70%) per chemical. Actually, the savings would be greater because most tests employ dose sighting studies.

Table 1. Potential reductions in animal usage in the U.S. HPV testing program

Human Health Toxicity Test (OECD #)	Sample Size (approx.)	Dose Sighting Study	Animal Savings Compared to Traditional Test (in bold)
ACUTE TOXICITY			
401 Acute oral toxicity	30	yes	
420 Fixed dose	20	yes	
423 Acute toxic class	9	no	
425 Up-and-down	8	no	22
REPRODUCTION/DEVELOPMENTAL TOXICITY			
415 One-generation reproduction toxicity	160	yes	
414 Teratogenicity	160	yes	
421 Reproduction/developmental toxicity screen	80	yes	240
28-DAY REPEATED DOSE TOXICITY			
407 Repeated dose 28-day oral toxicity	40	yes	
422 Combined repeated dose toxicity and reproductive/developmental toxicity screen	80 *	yes	40
MUTAGENICITY			
474 Mammalian erythrocyte micronucleus	50 2 sexes	yes	
422 Combined developmental toxicity screen with micronucleus test for males; females may need separate dosing.	30 2 sexes	yes	20
TOTAL ANIMALS REQUIRED			
Without use of reduction strategies	440		
With use of reduction strategies	118		
TOTAL SAVINGS OF ANIMALS WITH USE OF REDUCTION STRATEGIES			322 (> 70% reduction)

* same animals as would be used in OECD 421

APPENDIX D. Background on Ecological Risk Assessment.

Ecological risk assessment uses a hazard quotient (expected exposure divided by toxicity reference value) approach to characterize risk from exposure to xenobiotic substances. The toxicity benchmark used in calculating the hazard quotient is a chronic No Observed Adverse Effects Level toxicity endpoint. This endpoint is selected to reflect the assessment endpoint(s) in the risk assessment and can involve everything from survival of individuals to reproductive endpoints to biochemical function. Because of the wide range of receptor species that can be the focus of an ecological risk assessment, toxicity data for the benchmark is obtained from a variety of species, toxicity endpoints, and toxicity tests and is extrapolated to the species of interest. Consequently, there is no standard suite of toxicity tests that are routinely used in ecological risk assessment. As a result, regulatory authorities have developed a series of toxicity tests that they require during the process of evaluating ecological risk under a variety of scenarios.

There is an enormous variation in testing required of new chemicals in the United States mainly depending on which law or statute they are regulated under (Federal Insecticide Fungicide and Rodenticide Act (FIFRA), US EPA Toxic Substances Control Act (TOSCA), or neither). Such "testing" may range from "toxicology by analogy", that is, non-testing based upon structure-activity arguments, to "lifetime" testing for carcinogens in at least two species. Many international agencies have also developed minimally acceptable testing protocols for new chemicals or new formulations that involve substantial possible exposures, and we have been guided in our recommendations by the suggested testing protocols from California programs, the U.S. Environmental Protection Agency, and the Organization for Economic Co-operation and Development (OECD; cf. Figure 1 below in this Appendix).

As specified in the U.S. EPA Ecological Effects Test Guidelines (OPPTS 850.1000 Special Considerations for Conducting Aquatic Laboratory Studies, EPA 712-C-96-113, April 1996; http://www.epa.gov/opptsfrs/publications/OPPTS_Harmonized/850_Ecological_Effects_Test_Guidelines/Drafts/850-1000.pdf), the solubility and stability of the test material must be known for the conditions under which the testing will take place. The behavior of the additive and its components must be based on experiments conducted under the same conditions as those occurring during the tests including but not limited to:

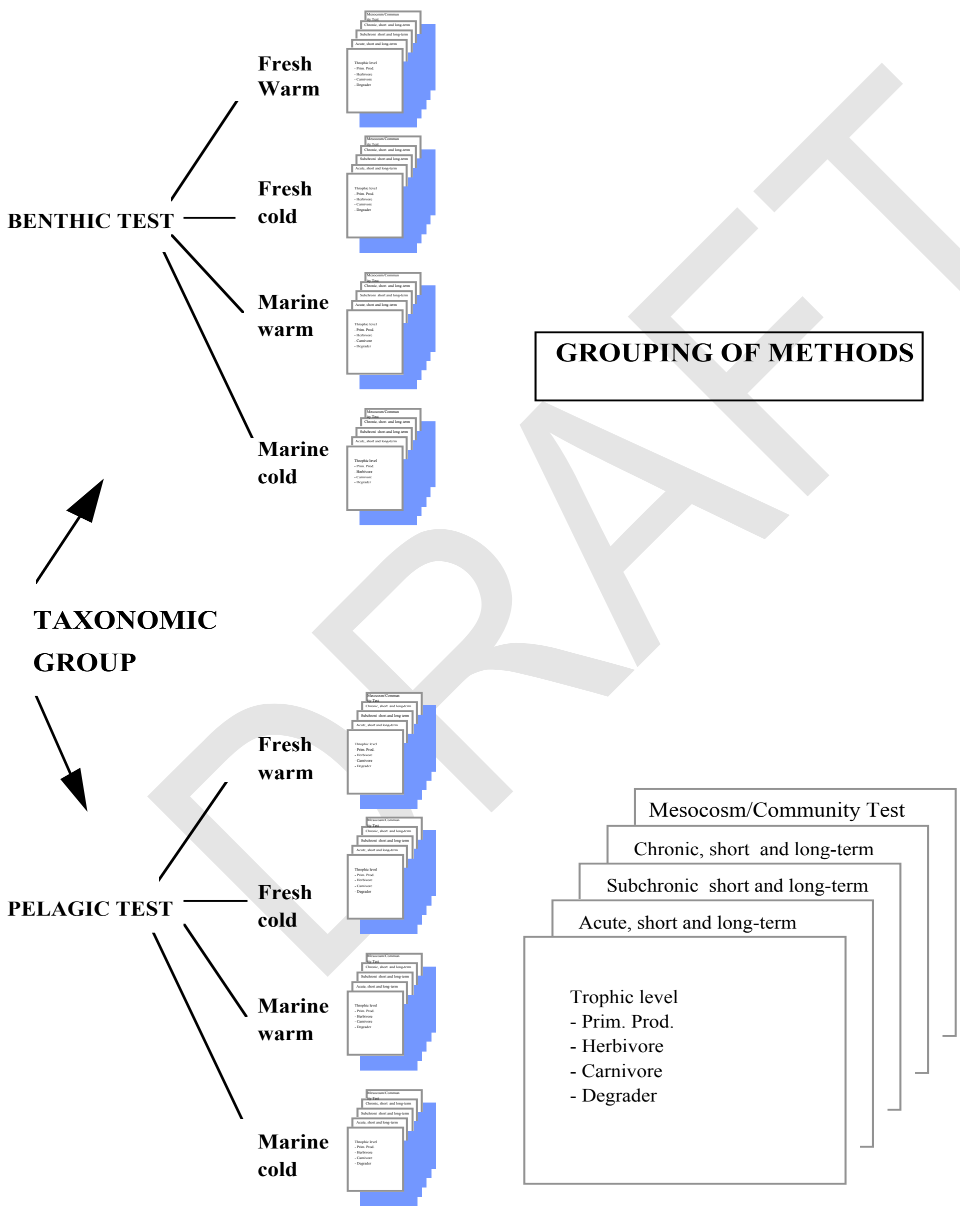
- Fresh or saltwater
- Temperature, pH, conductivity, lighting
- With test organism(s) in place
- Using the same test containers with the same test conditions (static/flow through)

Definitions of stability should follow the EPA guidelines. The concentrations of the chemicals must be measured at the beginning and the end of the toxicity test to determine their stability. If stability is a problem, tests should be conducted using static renewal techniques.

If solubility is a problem (<100 ppm), trials should be conducted using various solvents that are most likely to be effective and are recognized as being nontoxic. Other means should be employed to ensure that the appropriate methods are used during the laboratory tests to enhance solubility.

All toxicity tests must be performed using a sufficient number of replicates to provide the statistical power to detect statistically significant differences between the treatments and controls. Specific guidelines for performing the exposures (e.g., EPA manuals) may allow for a range of replicates to be used. However, the lower end of the range may not allow for valid statistical comparisons to be made, and the upper value of the range of replicates, or more, should be used. It may be noted that even if there are statistically significant differences between treatments and controls, the value of the endpoint for the treatment (e.g., survival) may be above the accepted threshold indicating that there is no biologically significant difference between the controls and treatments.

Figure 1 Evaluation strategy for aquatic toxicity testing methods[1]



[1] OEDC Series on Testing and Assessment #11. Detailed review paper on aquatic testing methods for pesticides and industrial chemicals. Part 1. Report ENV/MC/CHEM(98)19/Part 1, February 1998.

Table 1. Proposed tests for the evaluation of fuel additives.

Test group	Organism	Test length	Test Type	Endpoint
Freshwater Pelagic				
	Selenastrum capricornutum (green algae)	S	C	Cell growth
	Lemma gibba (higher plant)	S	SC	Growth
	Ceriodaphnia (water flea)	S	A	Survival
	Ceriodaphnia (water flea)	L	C	Life cycle – reproduction
	Pimephales promelas (fathead minnow)	S	A	Survival (96 hr)
	Pimephales promelas (fathead minnow)	L	C	Life cycle
Freshwater Benthic[1]				
	Hyalella azteca (amphipod)	L	A	Survival
	Hyalella azteca (amphipod)	L	SC	28,35,42 day survival
	Chironomus tentans (midge)	L	A/SC	Life cycle test (survival, growth, emergence)
Marine pelagic				
	Macrocystis pyrifera (giant kelp)	S	A	Spore germination and growth
	Stronglocentrotus purpuratus (Purple sea urchin)	S	SC	Fertilization (reproduction)
	Stronglocentrotus purpuratus (Purple sea urchin)	S	SC	Larval development
	Holmesimysis (mysid shrimp)	S	A	Survival
	Holmesimysis (mysid shrimp)	S	C	Survival and growth
	Atherinops affinis (Topsmelt)	S	A	Survival and growth (4 and 7 day)
Marine benthic[1]				
	Ampelisca abdita (amphipod)	L	A	Survival[2]

	Eohausteria estuarius (amphipod)	L	A	Survival
	Mytilus galloprovincialis (mussel)	L	C	Bioaccumulation
Terrestrial				
	Triticum aestivum (wheat)	S	A	Emergence, growth
	Brassica alba (mustard)	S	A	Emergence, growth
	Latuca sativa (lettuce)	S	A	Emergence, growth
	Eisenia foetida (earthworm)	L	SC	Survival, growth

[1] Spiked sediment, solid phase test
[2] *Ampelisca* is a tube burrowing organism; sediments must be fine-grained and should be of similar size to the environment in the exposure scenario

These tests are a subset of and consistent with the U.S. Environmental Protection Agency Office of Prevention, Pesticides and Toxic Substances (OPPTS) guidelines (http://www.epa.gov/opptsfrs/home/guidelin.htm) developed through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and which appeared in title 40, chapter I, subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS), and the guidelines published by the Organization for Economic Co-operation and Development (OECD). The marine tests proposed are a subset of and consistent with tests proposed under the California Ocean Plan Appendix III, Table III-1, http://www.swrcb.ca.gov/plnspols/oplans/docs/cop2001.pdf). It should be noted that the OPPTS requires 47 toxicity tests for hazard identification in the ecological risk assessment of pesticides.

APPENDIX E: The US EPA Office of Pollution Prevention and Toxics Tiered (OPPT) Approach to Exposure Assessment

OPPT uses a tiered approach to exposure assessment. Exposure assessments may use measured data or model estimates. Representative measured data of known quality are preferred over model estimates and are needed to validate and improve models. The EPA Guidelines for Exposure Assessment includes guidance on collecting and using monitoring data for exposure assessments. One of the goals in selecting the approach should include developing an estimate having an acceptable amount of uncertainty. In general, estimates based on quality-assured measurement data, gathered to directly answer the questions of the assessment, are likely to have less uncertainty than estimates based on indirect information (e.g., modeling or estimation approaches). For risk assessment purposes, a quantitative exposure assessment approach is needed and exposure information must be clearly linked to the hazard identification and dose-response relationship. The steps in the tiered approach are as follows:

Step 1. Gather Basic Data and Information for a Complete and Transparent Exposure Assessment.

Step 2. Develop a Screening Level Exposure Assessment.

Step 3. If Needed, Develop an Advanced Exposure Assessment.

These steps are explained in more detail below:

Step 1: Gather Basic Data and Information for a Complete and Transparent Exposure Assessment

Manufacturing/Processing/Use: The first step in assessing exposure for a chemical is to identify all of the manufacturing, processing and use activities for the chemical. This would include identifying all industrial, commercial and consumer uses.

Gather Measured Data: Monitoring or measured data may be available in a variety of resources, such as company records or databases, national databases, studies published in the open literature, references and other resources (e.g., for physical/chemical properties, fate, exposure factors, etc.) When obtaining measured or monitoring data, it is important to obtain all of the needed supporting information. Information on data quality objectives, the sampling plan, use of quality assurance samples, measurement of background levels, establishment and use of quality assurance and quality control measures, and selection and validation of analytical methods are important considerations when evaluating monitoring data or determining a strategy to collect additional monitoring data. The EPA Guidelines for Exposure Assessment includes additional information on these important considerations.

Estimates of Environmental Releases: Environmental release estimates are critical inputs for models that calculate indirect human exposures via the environment such as through ambient air or drinking water. They are also critical to modeling exposures to nonhuman aquatic and terrestrial species. Release estimates may be site-specific or they may be generic for a particular industrial process or industrial use. Releases from consumer and commercial products should also be estimated if applicable.

Potentially Exposed Human Populations: All potentially exposed populations should be identified. The exposed populations should be associated with the activity, task or source of environmental releases that leads to the exposure. Highly exposed or highly susceptible populations should be addressed whenever possible. Include all routes of exposure.

Chemical Properties and Fate: Reliable, measured values are preferred, and should be used when available. Measured values or estimates of water solubility and vapor pressure are important in evaluating whether a chemical will dissolve in water or exist as a vapor at ambient temperature, and are used to estimate worker and consumer exposures. Measured data or estimates of biodegradation, sorption, and volatilization potential are used to predict removal in wastewater treatment. Information on decay rates in the atmosphere, surface water, soil, and ground water are important in evaluating how long it takes a chemical to break down in the environment, and are used to estimate exposures to the general population and the environment.

Mitigation of Exposures: Process and engineering controls which are used to control exposures should be identified. Personal protective equipment (PPE) that will mitigate occupational exposures should be noted and quantitative estimates of exposure with and without the use of PPE should be provided.

Documentation of basic data and information: Document all measured data, environmental release scenarios, exposure scenarios, assumptions and estimation techniques.

Step 2: Screening Level Exposure Assessment

Purpose of a screening level exposure assessment: Screening level exposure assessments should be used to quickly prioritize exposures for further work.

Approach: A screening level exposure assessment will generate a quantitative conservative estimate of exposure. The screening approach generally involves using readily available measured data, existing release and exposure estimates and other exposure related information. Where conservative estimates of exposure are not available, simple models, which often use generic scenarios and assumptions, may be used to fill in gaps. For example, a screening-level model for ambient air exposure that is using generic assumptions may assume that the exposed populations live near the chemical release locations.

The exposure assessment should include a characterization of the exposure estimates. Guidance for characterizing exposure in EPA exposure assessments can be found in EPA's 1995 "Guidance for Risk Characterization."

Step 3: Advanced Exposure Assessment

Purpose of an advanced exposure assessment: An advanced assessment will develop more accurate estimates of exposure and will generally focus on the higher priority exposures identified in screening activities.

Approach: An advanced exposure assessment should quantify central tendency (e.g. median, arithmetic mean) and high end (i.e. greater than 90th percentile) exposures. A representative, well designed monitoring study of known quality is the ideal. Information on data quality objectives, the sampling plan, use of quality assurance samples, measurement of background levels, establishment and use of quality assurance and quality control measures, and selection and validation of analytical methods are important considerations when evaluating monitoring data or determining a strategy to collect additional monitoring data. The EPA Guidelines for Exposure Assessment includes additional information on these important considerations. Higher tier exposure models may also be used in advanced assessments. When they are used, every effort should be made to obtain accurate input data. For example, a higher tier model for ambient air exposure may use facility-specific parameters for emission rates, plant parameters such as stack height and exact location of the exposed populations.

The exposure assessment should include a characterization of the exposure estimates. Guidance for characterizing exposure in EPA exposure assessments can be found in EPA's 1995 "Guidance for Risk Characterization".

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General Notes: The approach described above is tailored to single chemical exposure assessments, although the general process could also be used for other types of hazards (e.g., biological hazards). Sometimes the focus of an exposure assessment will not be an assessment of human and ecological exposures to a single chemical across manufacturing, processing and uses. If the goal of the assessment is to identify safer substitutes for a particular use, the exposure assessment focus will be on all chemicals within that use (e.g., solvents used in a consumer product). In this case the basic data and information collected at the start of the assessment would need to be modified accordingly.

Exposure assessments may use measured data or model estimates. Representative measured data of known quality are preferred over model estimates and are needed to validate and improve models. OPPT encourages the appropriate use of our screening and higher tier models.

APPENDIX F. Background on biodegradation, with EU and US protocol examples.

Background on Biodegradation.

Both biotic and abiotic transformation processes may reduce the concentration and change the form of organic chemicals in the environment. Processes include chemical hydrolysis in surface and groundwater, photolysis in surface water and the atmosphere, and biodegradation (in waste water treatment, soils, sediments, surface and groundwater) (ECB). Usually sterilized (or "killed") controls are compared to nonsterile treatments to differentiate between abiotic and biodegradation. In some cases, e.g., for chemicals that undergo hydrolysis, the distinction between abiotic and biological degradation may be difficult to make.

Biodegradation is a critical process because it can significantly affect the fate of a pollutant in the environment. On one hand, biodegradation can result in the complete elimination of a chemical or, on the other hand, transformation of the chemical into a more harmful substance. Biodegradability is not a fixed property of a chemical, such as solubility or volatility, but is a function of environmental conditions and the microbial capabilities of a particular location.

Biodegradation is defined as the chemical alteration, by microbial metabolic processes, of one chemical into another chemical form. Biodegradation includes transformation ("primary degradation"), in which the original chemical is altered into another form of organic chemical, and mineralization ("ultimate degradation"), in which the original chemical is converted into carbon dioxide and other inorganic compounds (e.g. nitrate, ammonium, chloride). Mineralization is often associated with the growth of microorganisms, in which case carbon, and perhaps other elements, from the original chemical are converted into microbial cellular material. This possibility must be considered if biodegradation is estimated by measurement of a product, such as carbon dioxide, and there may not be a one-to-one conversion of the original chemical into its product. With transformation, there is potential for formation of a new organic chemical ("degradation product") that is toxic or behaves in some undesirable manner in the environment (e.g., more mobile). Thus it is critical to identify the chemical structures of the degradation products and, as appropriate, subject them to a multimedia assessment.

Biodegradation can also be coupled with the metabolism of second chemical, through a process called cometabolism, in which constitutive or induced enzymes capable of degrading this second chemical also can transform the chemical of interest. Cometabolism often has no benefit, and in some cases may be harmful to the microorganisms involved due to formation of toxic intermediate compounds (Alexander, 1999).

Biodegradation can occur under both aerobic and anaerobic (no oxygen present) conditions via different metabolic pathways and usually different types of microorganisms. Aerobic conditions are common in surface waters, soils and some groundwater aquifers. Anaerobic conditions are common in fresh and estuarine sediments, flooded soils, and many groundwater aquifers. The fact that a chemical can be degraded under aerobic conditions in no way ensures that it will degrade anaerobically, and vice versa, thus the test methods selected to measure biodegradation potential must reflect the environment into which the chemical will be released.

It is important to recognize that new fuels are actually mixtures of different chemicals, each of which has some potential to biodegrade. Mixtures are complicated by the fact that multiple chemicals interact with one another and can potentially change the biodegradation rate of another chemical present (Alexander, 1999). Interactions include toxicity, diauxy-type phenomena (where one chemical is used preferentially to another), stimulation (e.g., through supporting cometabolic reactions), and physical interactions (e.g., one chemical acting as a solvent for another). Unfortunately there has been only limited research on predicting the biodegradation of chemicals in mixtures, so not much is known about this potentially important fate phenomenon.

Biodegradation potential can be reduced if a chemical adsorbed to organic matter or clay and thus not physically available to microbial populations that would otherwise degrade it. The absence of biodegradation may not be a problem for exposure if it can be demonstrated that the sorbed form of the chemical is neither mobile nor toxic to receptors in the vicinity (Alexander, 1999).

European and US EPA Guidelines Summary.

1. The European Chemical Bureau (ECB has identified existing and defined new protocols for evaluation of the biodegradation potential of a chemical in the environment. The ECB recognizes that measured biodegradation potential data are important for multi media assessments. Data should be reliable and representative of the geographic and time scales of relevance, take into consideration sources and exposure pathways, and reflect relevant environmental concentrations (ECB).

2. The US EPA Office of Prevention, Pesticides and Toxics (OPPTS) www.**epa**.gov/**oppts**/ have consolidated and streamlined their test guidelines for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations. These Harmonized Test Guidelines

(Series 835 Fate, Transport and Transformation Test Guidelines -- Final Guidelines) are summarized in Table 1.

The Organization for Economic Cooperation and Development (OECD) environmental directorate calls for a tiered set of tests that measure the potential for a chemical to biodegrade. The tests range from the simplest, called the "ready biodegradation test" or the 301A series, to more complex tests that incubate the chemical longer and under different environmental conditions.

Estimation of biodegradation potential (or rates), e.g. through use of quantitative structure-activity relationships (QSAR), is not commonly utilized for most organic chemicals. In this case, structural analogs to the chemical of interest are used rather than the actual compounds to estimate biodegradation potential; however, selection of appropriate analogs must be made with considerable care. The determination of similarity of an analog should not be subjective but based on consideration of structure-activity data to demonstrate, for example, that the analog acts biologically like the additive component it was chosen to represent. This is not an easy task, however. For example, aliphatic compounds have a similar structure and are ultimately subjected to the same metabolic pathway. Aliphatic chain length, however, can significantly affect biodegradation rate, e.g., anaerobic, alkane-degrading bacteria have very specific size ranges of alkanes that they can degrade (e.g., some species degrade only C6 to C8, whereas others degrade only C14 to C20; Spormann and Widdel 2000). Such differences in molecular weight also have the potential to affect uptake and toxicity.

OPPTS Series 835 Test Guidelines

OPPTS Number	Name	Existing Numbers			EPA Pub. no.
		OTS	OPP	OECD	712–C–
	Series 835—Fate, Transport and Transformation Test Guidelines.				
	Group A—Laboratory Transport Test Guidelines.				
835.1110	Activated sludge sorption isotherm	none	none	none	96–298
835.1210	Soil thin layer chromatography	796.2700	none	none	96–047
835.1220	Sediment and soil adsorption/desorption isotherm	796.2750	none	106	96–048
	Group B—Laboratory Abiotic Transformation Test Guidelines.				
835.2110	Hydrolysis as a function of pH	796.3500	none	111	96–057
835.2130	Hydrolysis as a function of pH and temperature	796.3510	none	none	96–059
835.2210	Direct photolysis rate in water by sunlight	796.3700	none	none	96–060
835.2310	Maximum direct photolysis rate in air from UV/visible spectroscopy	796.3800	none	none	96–066
	Group C—Laboratory Biological Transformation Test Guidelines.				
835.3100	Aerobic aquatic biodegradation	796.3100	none	none	96–075
835.3110	Ready biodegradability	796.3180, .3200, .3220, .3240, .3260	none	301	96–076
835.3120	Sealed-vessel carbon dioxide production test	none	none	none	96–311
835.3160	Biodegradability in sea water	none	none	306	97–351
835.3170	Shake flask die-away test	none	none	none	96–297
835.3180	Sediment/water microcosm biogradation test	none	none	none	96–083
835.3200	Zahn-Wellens/EMPA test	796.3360	none	302B	96–084
835.3210	Modified SCAS test	796.3340	none	302A	96–085
835.3220	Porous pot test	none	none	none	96–301
835.3300	Soil biodegradation	796.3400	none	304A	96–088
835.3400	Anaerobic biodegradability of organic chemicals	796.3140	none	none	96–090
	Group E—Transformation Chemical-Specific Test Guidelines.				
835.5045	Modified SCAS test for insoluble and volatile chemicals	795.45	none	none	96–097
835.5154	Anaerobic biodegradation in the subsurface	795.54	none	none	96–098
835.5270	Indirect photolysis screening test: Sunlight photolysis in waters containing dissolved humic substances	795.70	none	none	96–099

There is good documentation of the effects of minor structural differences on biodegradability for certain compound classes [e.g., differences among xylene isomers; methylbenzene (i.e., toluene) versus ethylbenzene; Heider et al. 1998]. In conclusion, the QSAR approach has been relatively successful within narrow groups of chemicals of similar structure (Jaworska et al., 2003), but is not, as of yet, a broad predictive tool that can substitute for measured data.

References

Alexander, M. 1999. Biodegradation and bioremediation. 2nd ed. Academic Press, San Diego, CA.

Jaworska, J., Howard, P., and Boethling, R.S., 2003. Quantitative Structure Biodegradadation Relationships - A Review. Environmental Toxicology and Chemistry, 22(8):1710–1723, doi: 10.1897/01-302, pp. 1710–1723.

Spormann, A.M., Widdel, F., 2000, Metabolism of alkylbenzenes, alkanes, and other hydrocarbons in anaerobic bacteria. Biodegradation 11: 85–105.